# RUTHENIUM CYCLOHEPTATRIENYLIDENE CARBENE COMPLEXES, IRON CYCLOPROPYLIDENE CARBENE COMPLEXES. A NOVEL PHOTOINDUCED CYCLOPROPYLIRON/FERRACYCLOBUTENE REARRANGEMENT.

By

JAMES R. LISKO

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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"...an artist is a creative person driven by demons. He doesn't usually know why they chose him and he's usually too busy to wonder..."

William Faulkner

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August 1984

Chairman: William M. Jones
Major Department: Chemistry

Aromatic organotransition metal carbene complexes possess an intraligand 4n+2 $\Pi$-electron system. Recently, the syntheses of the dicarbonyl-$\eta^5$-cyclopentadienyliron and pentacarbonyltungsten carbene complexes of cycloheptatrienylidene was reported by this laboratory. These were the first aromatic carbene complexes (n=1) of a first and third row transition metal, respectively. The synthesis of dicarbonyl-$\eta^1$-cycloheptatrienylidene-$\eta^5$-cyclopentadienylruthenium hexafluorophosphate ($\overset{+}{R}pp=C_7H_6\ PF_6^-$) is the first aromatic organotransition metal carbene complex of a second row transition metal. The synthetic method, as noted for the iron case, was also readily applicable to the

preparation of two benzannelated aromatic carbene complexes (n=2): dicarbonyl-$\eta^1$-4,5-benzacycloheptatrienylidene-$\eta^5$-cyclopentadienylruthenium hexafluorophosphate ($\overset{+}{R}p=C_{11}H_8$ $PF_6^-$) and dicarbonyl-$\eta^1$-3,4-benzocycloheptatrienylidene-$\eta^5$-cyclopentadienylruthenium hexafluorophosphate ($\overset{+}{R}p=C_{11}H_8'$ $PF_6^-$). The phosphinylated ruthenium carbene complex, carbonyl-$\eta^1$-cycloheptatrienylidene-$\eta^5$-cyclopentadienyltributylphosphine-ruthenium hexafluorophosphate ($\overset{+}{R}pp=C_7H_6$ $PF_6^-$) was prepared and the barrier to rotation about the metal carbon multiple bond was determined to be 8.49 kcal/mole. The carbene carbon resonances ($^{13}C$ NMR) and rotational value for the metal carbon multiple bond of the ruthenium carbene complexes were compared with the appropriate iron analogues.

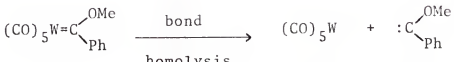
Cyclopropyliron sigma complexes have been allowed to react with hydride abstractors to give allene complexes, presumably via intermediate cyclopropylidene carbene complexes. The optically active cyclopropyliron complex, dicarbonyl-$\eta^5$-cyclopentadienyl(1-methoxy-trans-2,3-dimethylcyclopropan-1-yl) iron, was allowed to react with the potent methoxy abstractor trimethylsilyltrifluoromethanesulfonate (TMSOTF), thus unambiguously generating the cyclopropylidene carbene complex, dicarbonyl-$\eta^5$-cyclopentadienyl-$\eta^1$-trans-2,3-dimethylcyclopropylideneiron triflate. From the apparent lack of optical activity in the product allene complex, ($\eta^2$-2,3-butadiene)-dicarbonyl-$\eta^5$-cyclopentadienyliron triflate, the most likely mechanism for the conversion of cyclopropylidene to allene

complex involves a disrotatory ring opening to generate an allyl cation species which collapses to the allene complex.

Photolysis of the previously mentioned methoxy substituted cyclopropyliron complex or the analogous acyl complex, dicarbonyl-$\eta^5$-cyclopentadienyl(1-methoxy-trans-2,3-dimethylcyclopropyl-1-carbonyl)iron, results in formation of the novel ring expanded carbene complex, 2-(carbonyl-$\eta^5$-cyclopentadienyliron)-3-methoxy-trans-4,5-dimethylcyclopent-2-en-1-one, presumably via a metallocyclobutene complex. The proposed mechanism involves migration of alkyl from carbon to 16-electron coordinately unsaturated iron, thus generating the metallocyclobutene complex which subsequently ring expands to give the novel metallocyclopentenone.

# CHAPTER I
# INTRODUCTION

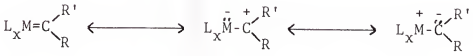
Organotransition metal carbene complexes, the first of which was prepared by E. O. Fischer in 1963, may be defined as those compounds containing a metal-carbon double bond where homolysis of such bond would result in a coordinately unsaturated metal fragment and a divalent carbene-type carbon with its associated groups.[1] Though this is illustrated for Fischer's original carbene complex 1, it must be noted that this type of bond homolysis has




1 2 3

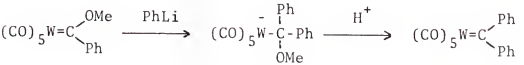
never been conclusively observed. Since Fischer's synthesis of 1, literally hundreds of carbene complexes have been prepared. Indeed, several lengthy review articles are in the current literature.[2-4] Virtually all of the early carbene

complexes appeared to have an electrophilic carbene carbon, presumably due to the large contribution of resonance form 5 to the total electronic state of the molecule.



4 5 6

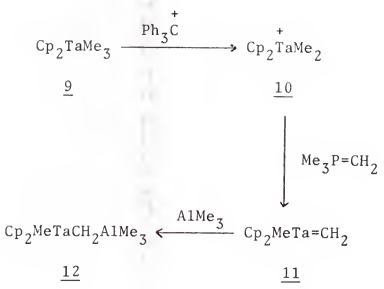
Casey et al. used this behavior in the preparation of 8 from 1 via the intermediate anionic complex 7.[5,6]



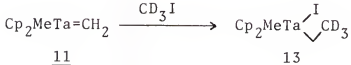
1 7 8

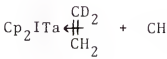
More recently, some carbene complexes have been prepared in which resonance form 6 appears to dominate. For example, Schrock prepared the novel methylidene complex 11 as outlined below.[7] This carbene complex was shown to be inert

to nucleophiles; however it reacted quite readily with electrophiles (e.g. $AlMe_3$) at the carbene carbon,

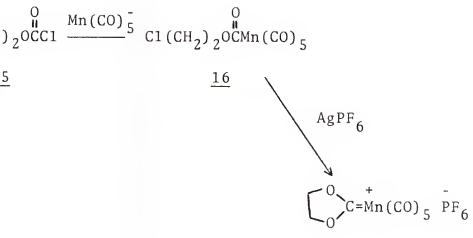



as exemplified by the isolation of the $AlMe_3$ adduct 12. Indeed, 11 even reacts with methyl iodide-$d_3$ to give 14 presumably via 13.

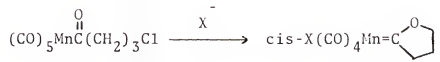


With the evolution of transition metal carbene complexes, some attention has been focused on complexes of cyclic carbenes. In many cases, such as 17 and a closely related analogue 19, the presence of the ring is trival.[8,9]




15 16 17




18 19

However, if the ring is completely unsaturated, its presence becomes important to the properties of the complex. Thus, depending on the number of double bonds, the metal, and its associated ligands, potential aromaticity and

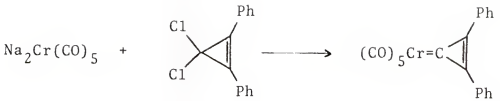
antiaromaticity may have a profound impact. For instance, carbene complexes of metal systems in which resonance form 20 tends to dominate should give stable complexes of 21 which a=1,3,5...(odd integers), while those of 21 in which resonance form 22 is dominant would then give stable complexes where a=2,4,6...(even integers).

20

21

22

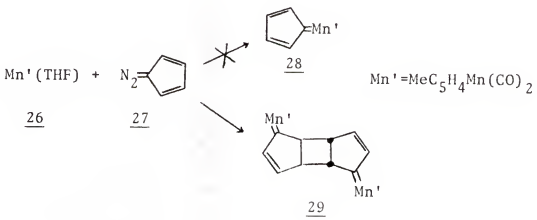
Metal complexes of cyclic, conjugated carbene complexes are relatively rare. Examples of those in which a=1 and resonance form 20 is of importance have been found to be extremely stable. Ofele prepared 25 by the action of a metal dianion 23 on the cyclopropenyl dihalide 24.[10]




23 24 25

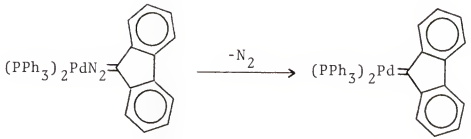
As would be expected, attempts to prepare cyclopentadienylidene complexes (21, a=2) in which 20 is of some importance have not led to stable compounds.

Hermann isolated 29 from the attempted preparation of 28. Presumably, if 28 was initially formed it was simply too reactive and therefore dimerized.[11]




26 27 28 29

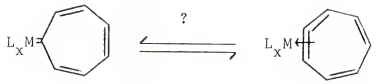
Nakamura isolated 31 from the thermolysis of diazo-complex 30.[12] Though the carbenic moiety is a benzannelated cyclopentadienylidene, one assumes that this is a compound of type 21 (a=6) with a contribution from resonance form 22, i.e., having partial aromatic character.




30 31

It seems, then, that there has been no definitive evidence for the isolation of an antiaromatic carbene complex, though a few (including this author) have attempted such a preparation.

Metal complexes of cyclic, conjugated carbenes of type 21 where a=3 are especially interesting because in these cases the ring is large enough to accommodate a valence isomeric allene form 33. This possibility is intriguing because there is clear evidence that the allene 35 is of

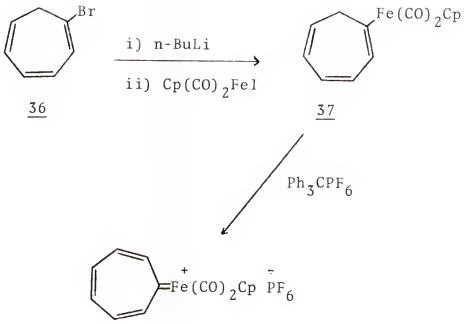



32 33

lower energy than the carbene 34 in the uncomplexed form.[13]

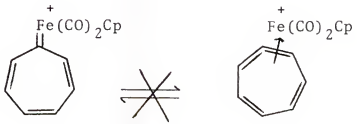
34 35

In this laboratory, complex 38 was prepared via hydride abstraction from 37, which was prepared in the manner illustrated.[14]



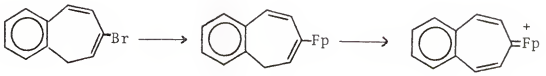

36 37 38

Via $^{1}H$ NMR, $^{13}C$ NMR, and most recently x-ray analysis, it has been determined that compound 38 exists in the carbene form in both solution and solid state and not as the allene complex 39.[15]




38 39

The effect of benzannelation upon the structural preference was probed by preparing 42 in the manner previously illustrated for 38. Again the complex was found to have the carbene structure 42 rather than the



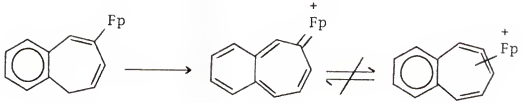

40 41 42

metal coordinated allene 43.


42 43

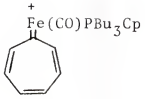
Calculations predict that benzannelation of cycloheptatrienylidene, as in 44, should increase the separation between carbene 44 and allene 45 by 79.2 kcal/mole.[16] It was therefore most astonishing that treatment of 46 with trityl cation gave rise to complex 47, where the aromaticity of the benzene ring has been interrupted, rather than the allene 48.

44 45




46 47 48

The carbene/allene preference in Fe(II) complexes was further investigated in this laboratory by Manganiello et al., who found that substitution of one carbonyl by $PBu_3$ in 38 and 42 still resulted in only the carbene complexes 49 and 51 rather than the respective allene complexes 50 and 52.[17]

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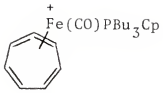


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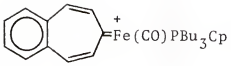


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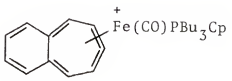


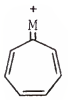

52

Interestingly, barriers to rotation about the Fe-C bond of 9.6 and 10.3 kcal/mole were observed for 49 and 51, respectively. This has been interpreted as evidence for an electronic component in the activation barrier to rotation, an interpretation that has sound theoretical basis.[18]

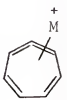
The question then arises: would going down the periodic table from Fe to Ru to Os cause the allene structure to be preferred? A priori this is virtually impossible to answer

because what is known about bonding trends as one moves down a triad does not provide an unambiguous prediction. For instance, the reasonable argument can be made that the allene form should be favored by moving down a triad because pi-bond strengths increase in that order.[19] However, it appears that sigma bond strengths increase in the same order (which would favor the carbene structure) and the thermodynamic data necessary to decide which is more important in the Fe, Ru, Os triad is not available.[20]

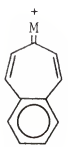
We therefore thought it would be interesting to prepare Ru and Os complexes of cycloheptatriene and benzannelated cycloheptatriene 53a - 58d to determine if cases might be found where cycloheptatetraene complexes would be favored over the carbene form. In the event that the carbene



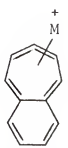
53a-d



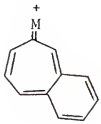
54a-d



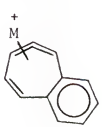
55a-d



56a-d



57a-d



58a-d

$Cp(CO)_2Ru$: (53-58)a

$Cp(CO)PBu_3Ru$: (53-58)b

$Cp(CO)_2Os$: (53-58)c

$Cp(CO)PBu_3Os$: (53-58)d

structure was favored in all cases, it would be most interesting to compare the physical properties of the Ru and Os complexes with those of Fe with special interest in information about back-bonding.

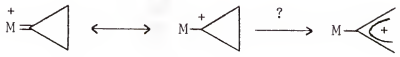
The concept of an equilibrium between a carbene and allene complex, as mentioned for 32 and 33 respectively, is not limited to complexes where the carbenic ligand is both cyclic and conjugated. Indeed, the only prerequisite to observe such a phenomenon would be the presence of an organic fragment containing three carbons, the minimum necessary for an allene complex such as 59; however, this three carbon allenic fragment would by necessity dictate that the valence isomer carbene complex be both cyclic and saturated, vis cyclopropylidene complex 60. Interestingly enough though, another valence isomer, neither carbene nor allene, presents itself: the metal-substituted allyl cation 61.


59


60

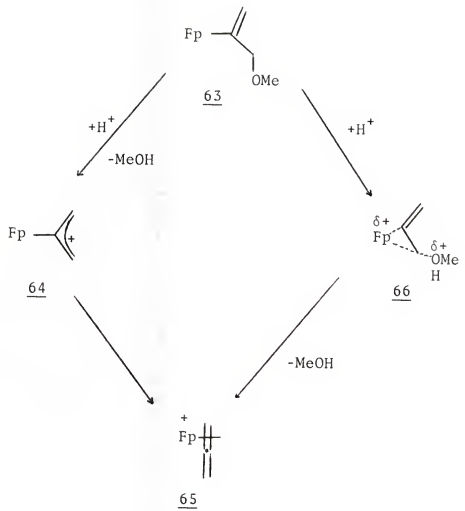

61

One can not help but notice that a resonance structure of 60 is 62, a metal-substituted cylcopropyl cation which from an organic chemist's standpoint should ring-open to the aforementioned metal-substituted allyl cation 61.

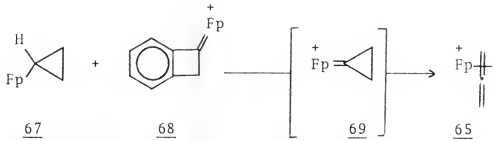



60 62 61

Since the nature of backbonding in a carbene complex has been viewed as a metal HOMO/carbene carbon LUMO interaction, compound 61 is afforded no stabilization by being bound to the metal and therefore could rearrange to the lower energy 59. Rosenblum et al., has found that the protonation of 63 results in formation of the allene complex 65, either via a discrete intermediate such as the metal-substituted allyl cation 64 or a concerted process involving assistance from the Fe-C bond during the loss of methanol as illustrated by 66.[21]

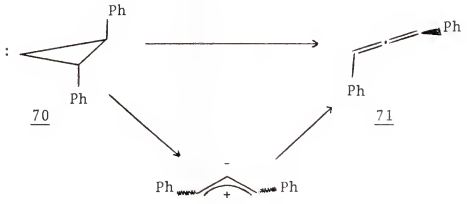



Giering et al. has treated 67 with 68 and obtained 65 possibly via the cyclopropylidene complex 69.[22]




67 68 69 65

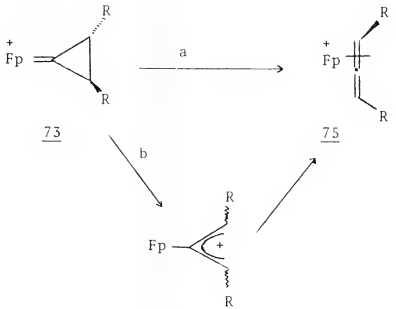
One could surmise that 69, if formed, rearranged to 65 possibly via the aforementioned 64; however, in uncomplexed cyclopropylidenes, Jones and Walbrick have shown that optically active 70 collapses to optically active 71, thus implying a concerted process rather than one involving an achiral intermediate such as 72.[23]




70 71

72

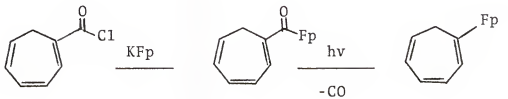
EHMO calculations by Winchester have shown that 69 is of higher energy than 65, with 64 lying at some intermediate level.[24] From these calculations and the experimental work of Rosenblum, Giering, and Jones et al. one then realizes that if the cyclopropylidene complex 73 could be unequivocably generated in optically active form, one would then be in a position to evaluate the mechanism of ring-opening of 73.[21,22,23] The optical purity of



allene 75 would let one determine whether path a (a concerted ring-opening leading directly to allene 75 or path b (a stepwise opening to the achiral allyl cation 74 and subsequent formation of 75) was the lower energy route of 73 to 75. It was the aim of this research to unambiguously prepare 73 in optically active form and determine the stereochemistry of its conversion to 75 thus establishing the mechanism for the ring-opening of cyclopropylidene carbene complexes.

## CHAPTER II
## RESULTS AND DISCUSSION

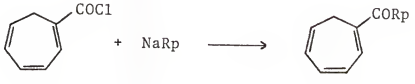
The synthesis of compound 53a, the first cycloheptatrienylidene carbene complex featuring a second row transition metal, was attempted initially via a route that had not originally been used to prepare the $F_p$ analogues. Jones had found that reaction of 76 with $KF_p$ resulted in formation of the acyl complex 77, which could be smoothly decarbonylated to give the σ-complex 37.[25] The primary advantage of this method over the previously mentioned route




76 77 78

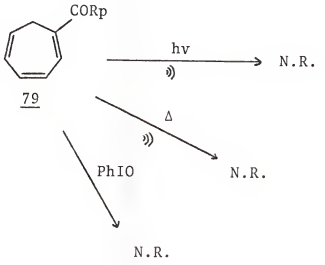
using the appropriate alkylithium is that the acyl complex 77 is thermally stable; therefore, larger quantities could be prepared and stored over long periods of time.

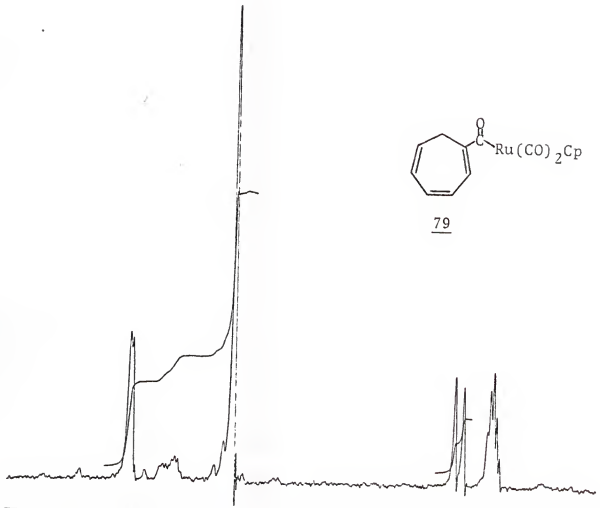
The reaction of freshly prepared sodium dicarbonyl-$\eta^5$-cyclopentadienylruthenate 78 (NaRp) with acid chloride 76 resulted in the isolation of crystalline acyl complex 79.




76 78 79

As shown in Figure 1, the acyl complex exhibits a doublet at δ2.35 indicative of a 1-substituted cycloheptatriene; however, photolysis of 79 in benzene was fruitless as the acyl complex appeared to be stable under conditions which quantitatively decarbonylate the iron analogue 77. Furthermore, photolysis, thermolysis with ultrasound and chemical decarbonylation methods gave the same result: no decarbonylation. The sigma complex 80 was then prepared by the

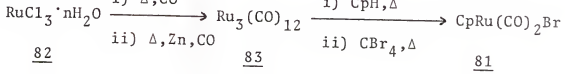


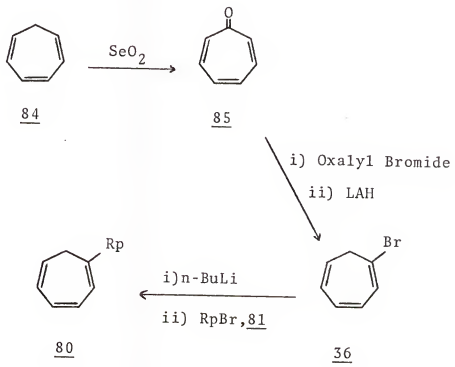



79

Figure 1. 60 MHz $^{1}H$ NMR Spectrum of Compound 79

method previously used in the synthesis of the iron sigma complex 37; however a new method was used in the preparation of the ruthenium halide 81.[26]

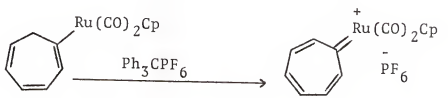



Unlike the iron sigma complex 37, which happens to be a mixture of the 1-,2-,and 3-isomers, compound 80 appears to be a mixture of the 1-isomer with either the 2- or 3-isomer present in a somewhat lesser amount. It seems that the

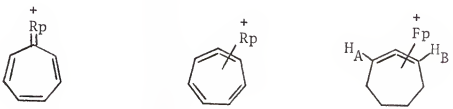
ruthenium halide 81 is more selective than the analogous iron halide.

Treatment of the sigma complex mixture 80 with trityl hexafluorophosphate gave a new complex, as seen in Figure 2, that was shown to be the carbene complex 53a, rather than the allene 54a from the following properties.




80 53a

The presence of only the carbene in the solution state is deduced from the $^1H$ NMR spectrum. Quite analogous to the iron carbene complex 38, the ruthenium-complexed cycloheptatrienylidene ligand shows resonances at δ 7.90-8.35(m,2H), 8.40-8.70(m,2H), and 9.90(d,2H) indicative of 53a and not the less symmetric allene complex 54a.




53a 54a 86

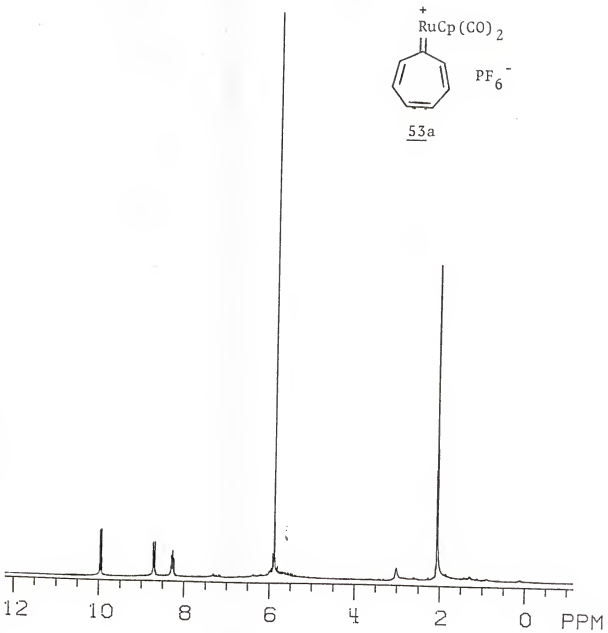
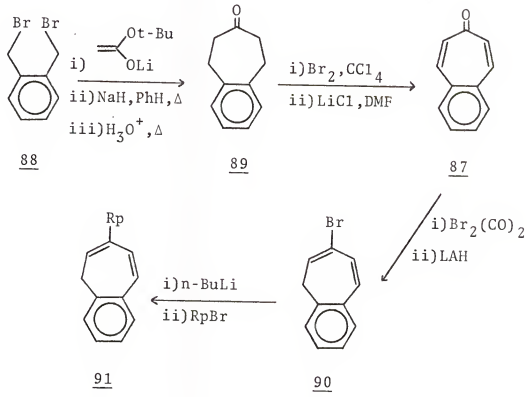


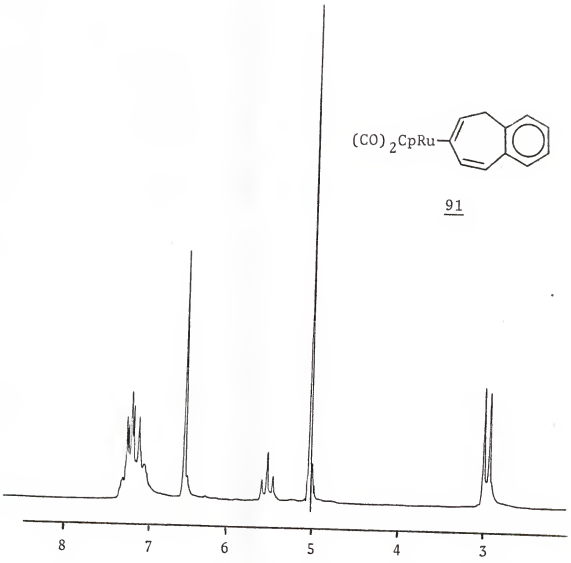

Figure 2. $^{1}H$ NMR Spectrum of Dicarbonyl-$\eta^{1}$-cycloheptatrienylidene-$\eta^{5}$-cyclopentadienylruthenium Hexafluorophosphate 53a.

Indeed, drawing an analogy between 54a and the recently prepared 86, one would expect $\delta H_A \approx 6.5$ and $\delta H_B \approx 4.5$ if the ruthenium allene complex 54a were present.[27]

To prepare the benzannelated sigma complex 55a, the method of Paquette was used to synthesize 87, which was then converted to the halide via the method of Fohlisch et al.[28,29]



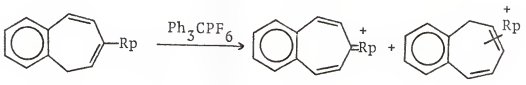

Treatment of the halide with n-BuLi followed by quenching with RpBr 81 resulted in isolation of the ruthenium sigma complex 91 as shown in Figure 3. The most striking feature in the $^1H$ NMR spectrum of 91 is




91

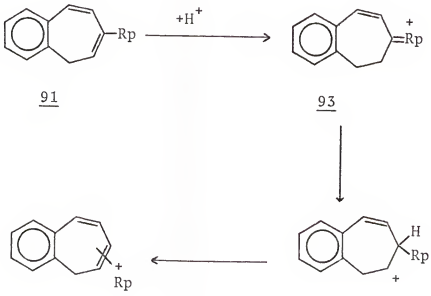
Figure 3. 100 MHz $^{1}H$ NMR Spectrum of Compound 91.

singlet at $\delta$6.58 which results from vinyl hydrogens on $C_2$ and $C_3$. This accidental equivalence is exactly the same phenomenon seen in the analogous iron complex 41. Treatment of sigma complex 91 with trityl hexafluorophosphate resulted in isolation of the carbene complex 55a rather than the allene complex 56a, though quite often the carbene complex 55a appeared to be

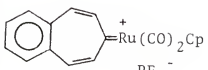



91 55a 92

contaminated with 92, presumably from acid-induced rearrangement of the sigma complex 91.




91 93 94 92




55a

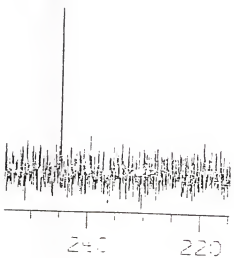
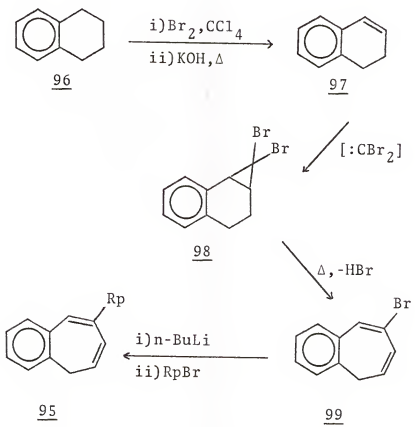
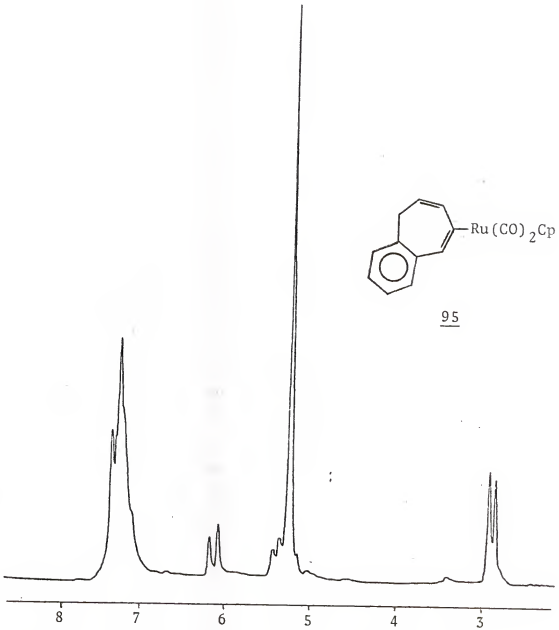



Figure 4. 75 MHz $^{13}C$ NMR Spectrum of the Low Field Region (215-250 ppm) of Compound 55a.

Finally, sigma complex 95 was prepared by the route analogous to that used for the synthesis of the iron complex 46. The bromoalkene 99 was prepared by the method of Waali.[30] Subsequent reaction of 99 with



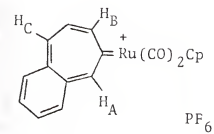

n-BuLi followed by quenching with RpBr gave rise to the ruthenium sigma complex 95, as shown in Figure 5. Upon treatment of 95 with trityl hexafluorophosphate, the presence of only the carbene complex 57a was detected; there was no indication of 58a by $^{1}H$ NMR analysis, as seen in Figure 6.




95

Figure 5. 100 MHz $^{1}H$ NMR Spectrum of Compound 95.

| H | ppm |
|---|---|
| A: | 10.171 |
| B: | 9.699 |
| C: | 9.120 |




57a

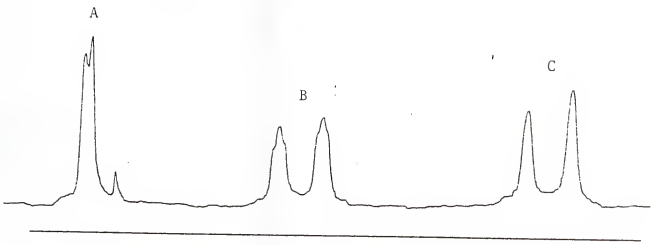
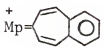


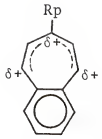

Figure 6. 100 MHz $^{1}H$ NMR Spectrum of the Low Field Region (9.0-10.5 ppm) of Compound 57a.

It appears that the ruthenium carbene complexes mimic the behavior of their previously discovered iron analogues; however, the $^{13}C$ NMR reveals a somewhat interesting and surprising effect in going from Fe to Ru. As seen in Table 1, it appears that the ruthenium carbene carbon resonance is approximately 20 ppm upfield from the analogous iron carbene carbon. Indeed, it appears that the carbene resonances in the ruthenium case can be explained by

Table 1. $^{13}C$ NMR Carbene Carbon Resonances (Fe vs. Ru)

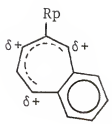
| Type | Fe | Ru |
|---|---|---|
|  | 242.3 | 223.6 |
|  | 265.9 | 244.7 |
|  | 201.0 | 186.6 |

classical resonance theory, as discussed by Allison for the iron analogues, i.e. the more localized (larger coefficient) the charge on a particular carbon, the further downfield will be the $^{13}C$ resonance as shown for the ruthenium carbene complexes.[31]



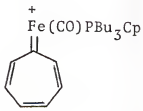

55a


53a

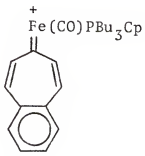



57a

Manganiello had prepared compounds 49 and 51 by $PBu_3$ substitution of one of the CO's in 38 and 42 respectively. This did indeed perturb the symmetry of the molecule as well as affecting the degree and conformation of backbonding.[17]

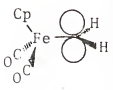



49

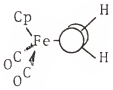



51

Hoffman et al. predicted carbenes complexed to symmetrically substituted transition metals such as Fp could exist in two conformations: bisected 100 and upright 101, the latter being 6.2 kcal/mole lower in energy.[32] Though the cycloheptatrienylidene carbene complexes show a bisected




100

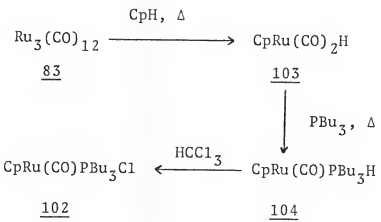



101

conformation in the solid state, the addition of the phosphine ligand destroys the symmetry about the iron and possibly increases the barrier to rotation by increasing the amount of backbonding from the metal to the carbene carbon. Indeed, the $^{13}C$ carbene carbon resonance of 49 lies at 278.8 ppm, approximately 36.5 ppm downfield from the parent 38. This downfield shift has been attributed

to an increase in backbonding. The rotational barriers in 49 and 51 were determined to be 9.8 and 10.6 kcal/mole respectively. Clearly, the increase from 9.8 to 10.6, kcal/mole must be electronic as the benzannelated fragment of 51 is removed from steric interaction with the Fp moiety.

The preparation of the ruthenium analogues of 49 and 51 was carried out in the following manner. As the acyl complex 79 was photostable, it seemed that the phosphinylated ruthenium halide 102 would be reacted with the appropriate alkyllithium. Based on recent work by Humphries and Knox and Rowan and Howell, the desired halide was prepared by the method illustrated below, the $^{1}H$ NMR of which is shown in Figure 7.[33,34] The new hydride 104, exhibited a resonance at




δ-12.5 (d, $^{2}J_{PH}$=25.4Hz) indicative of a phosphine substituted metal hydride. Reaction of 102 with a mixture of

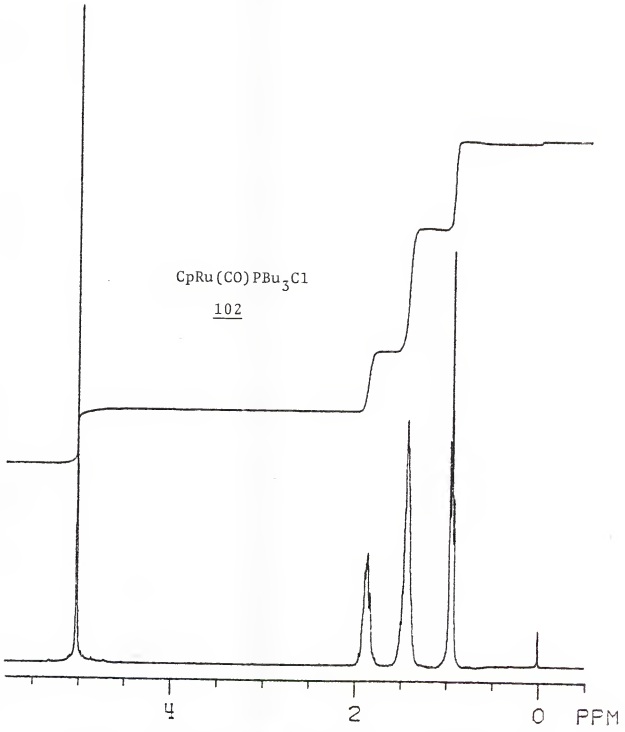
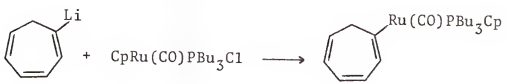



Figure 7. 300 MHz $^{1}H$ NMR Spectrum of Compound 102.

1-,2-, and 3-lithiocycloheptatrienes resulted in isolation of sigma complex 106 solely as the 1-isomer, as seen in Figure 8.




105 102 106

Again we see ruthenium being somewhat more selective than the iron analogue. Furthermore, the selectivity is quite analogous to work by Kawada and Jones, who observed the formation of only the 1-isomer 107 upon reaction of $\bar{W}(CO)_5Br$ 108 with a mixture of 1-,2-, and 3-lithiocycloheptatrienes.[35]

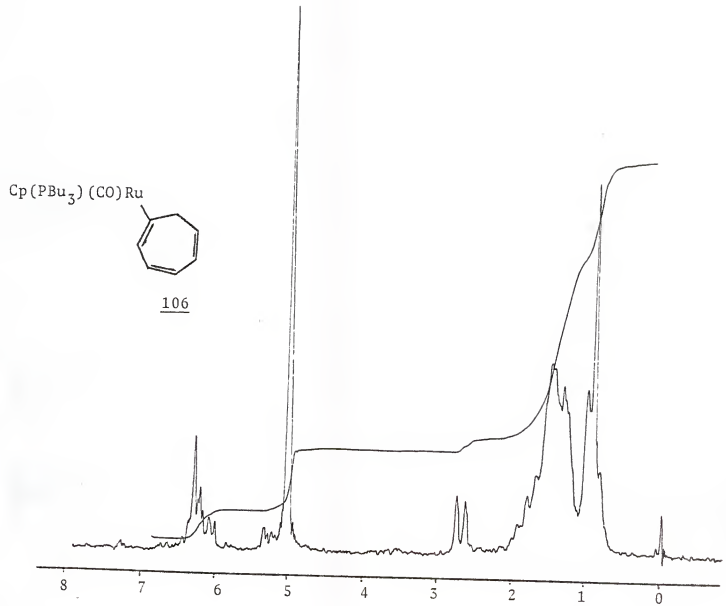
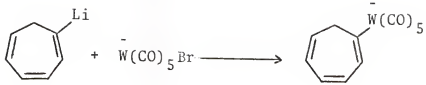
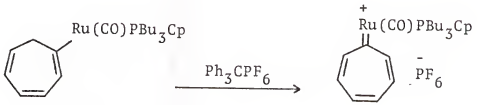



Figure 8. 60 MHz $^{1}H$ NMR Spectrum of Compound 106.

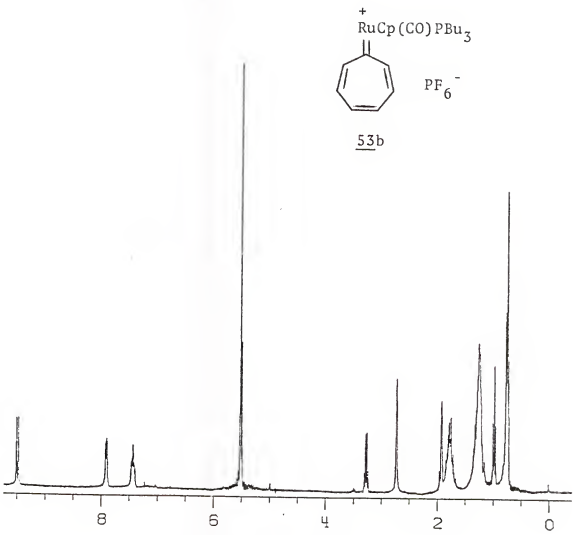



105 108 107

Treatment of sigma comples 106, with trityl hexafluorophosphate gave the carbene complex 53b as a deep red crystalline solid, the 300 MHz $^1$H NMR which is shown in




106 53b

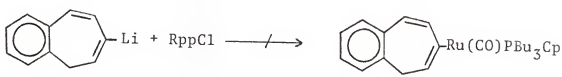



53b

Figure 9. 300 MHz $^{1}H$ NMR Spectrum of Compound 53b.

Figure 9 (MeOH has been added for temperature calibration according to the method of Van Geet[36]). As shown in Figure 10, irradiation of the multiplet at 7.45 ppm resulted in a collapse of the doublet at 9.50 ppm and the doublet of doublets at 7.90 ppm to singlets, thus establishing the identities of $H_{2,7}$, $H_{3,6}$, and $H_{4,5}$ as the resonances at 9.50, 7.45, and 7.90 ppm respectively.

Upon irradiation of $H_{3,6}$, $H_{2,7}$ may be expected to become non-equivalent singlets as the sample is slowly cooled. Indeed, as Figure 11 illustrates, one finds that the singlet at 9.50 ppm becomes two singlets with a coalescence temperature of -92.2°C, which reflects a $\Delta G^{\ddagger}$=8.49 kcal/mole, as calculated by the equation $\Delta G^{\ddagger}=RT_c(\ln T_c/\delta v+22.96)$.[37] Unfortunately, the preparation of the benzannelated ruthenium carbene complex 55b was unsuccessful in that sigma complex 110 was never isolated from the reaction of alkyllithium 109 with 102.




109 102 110

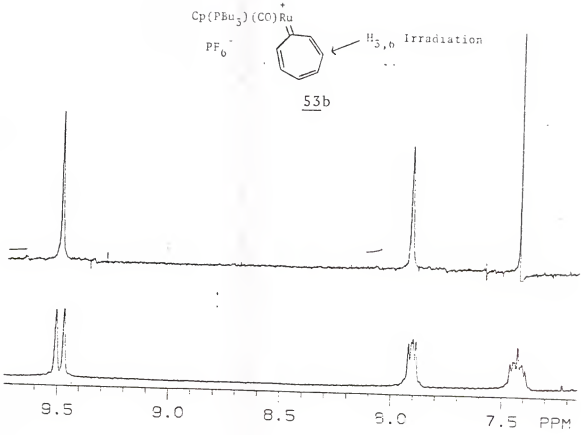



Figure 10. 300 MHz $^{1}H$ NMR Spectrum of Compound 53b with Irradiation of $H_{3,6}$.

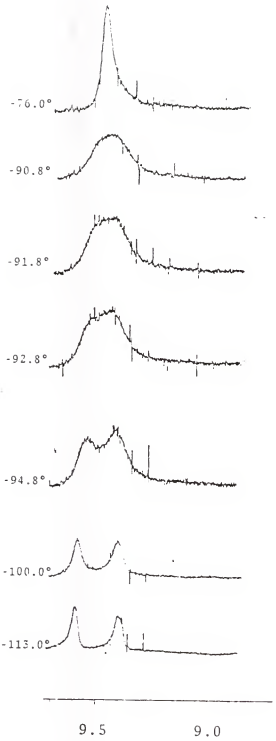
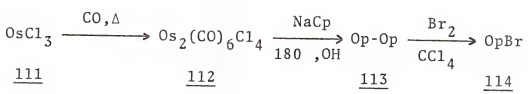



Figure 11. 300 MHz $^{1}H$ NMR Spectrum of Compound 53b with Irradiation of $H_{3,6}$ and Determination of Temperature of Coalescence.

Whether this is again due to the selectivity of the ruthenium or decomposition of 110 is purely conjecture.

The rotational barrier of 8.49 kcal/mol for 53b is somewhat lower than the value of 9.6 kcal/mol for 49. This may be due to a lesser degree of backbonding in 53b; however, a steric factor may contribute to this difference as going from Fe to Ru typically results in an increase of 0.1 Å for the metal-carbon bond. Furthermore, the chemical shift difference of 32.7 ppm in going from 53a to 53b is somewhat less than the value of 36.5 ppm as previously mentioned for the iron analogues 38 and 49. It appears then that the degree of backbonding in 53b as probed by the rotational energy barrier and the aforementioned carbene carbon shift differences is less than that observed in the iron analogue 49.

The preparation of the osmium starting materials was attempted in the following manner.




111 112 113 114

Op=$C_5H_5(CO)_2Os$

The preparation of 112 was reported by Manchot and Konig and reproduced quite easily; however, the reductive substitution of 112 to give the dimer 113 was not successful according to the procedure of Fischer et al.[38,39]

$$Os_2(CO)_6Cl_4 \xrightarrow{\quad / \quad} Cp(CO)_2Os\text{-}Os(CO)_2Cp$$

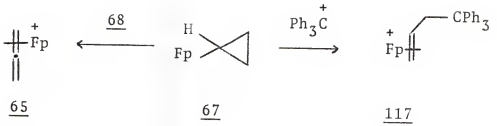
112 113

As the starting materials could not be prepared, attention was then turned to the preparation of novel cyclopropylidene carbene complexes.

The preparation of 115 presented a unique synthetic challenge: neither the optically-active cyclopropylidene carbene complex nor several of the possible key organic intermediates had been previously prepared. Upon retrosynthetic analysis, one immediately realizes that 115 would most likely be prepared from the sigma complex 116; however, the choice of leaving group $X^-$ is not so obvious.

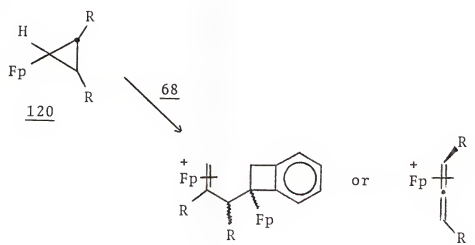

115 116

Giering, as previously mentioned, had treated the cyclopropyl sigma complex 67 with the quite selective hydride abstractor 68.[22] In this case, the allene complex 65 was isolated but no information concerning the mechanism of ring-opening was obtained. Giering et al. also found that 67, upon reaction with trityl cation, gave the ring-opened π-complex 117 instead of the expected hydride-abstraction allene product 65.



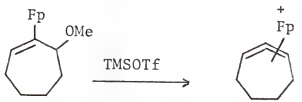

65 67 117

If this difference in product formation is due primarily to steric interaction between the hydride abstracting agent and the sigma complex, then one is led to conclude that the desired introduction of alkyl groups at the 2- and 3- position of the cyclopropane ring might favor the π-complex addition product 118 rather than the allene 119. For this reason it was felt that hydride would not be a good leaving group to generate cyclopropylidene carbene complexes.



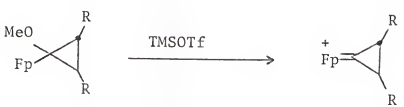

120 118 119

Recently in our laboratory, the use of trimethylsilyl trifuloromethanesulfonate (TMSOTf) in the clean abstraction of the methoxy function has met with great success. For example, the addition of one equivalent of TMSOTF to 121 results in quantitative formation of analytically pure allene complex 86.[27]




121 86

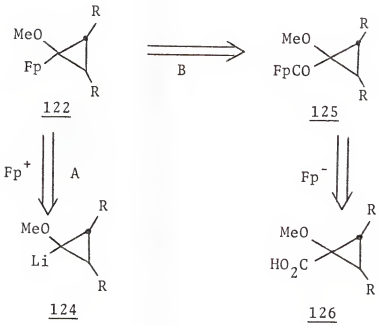
From the results, it was deemed that the use of a methoxy group as X would give the desired cyclopropylidene carbene complex. The remaining problem was in the choice of the R groups. Since steric bulk about the carbenic carbon should be kept to a minimum, yet the molecule must be chiral, the obvious (alkyl) choice of R would be a methyl group. It was felt that for a mechanistic study, the methyl group




122 123

would offer the least perturbation compared to other possible alkyl groups.

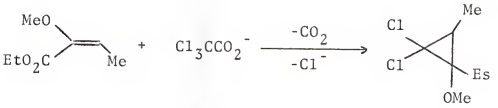
A retrosynthetic analysis of the sigma complex is somewhat straightforward in light of the known methods of generation of sigma complexes.




Through alkyllithiums have been found to react with Fp halides to give sigma complexes (analysis A), the yields are usually dismally low. Furthermore, the need for an optically active cyclopropyl sigma complex is more easily satisfied by going through the cyclopropanecarboxylic acid (analysis B). Indeed, several cyclopropane acyl complexes have been prepared in this laboratory.[40]

As analysis B provides the appropriate route, one is then left with determining the method of preparation of the α-methoxycyclopropanecarboxylic acid 126.

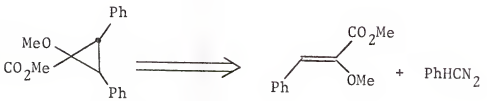
Upon reviewing the literature one realizes that α-methoxycyclopropanecarboxylic acids are somewhat rare. The only known preparation at the time this research was begun was that of Ando et al. using the carbene precursor 127 and the alkene 128 in a cycloaddition reaction.[41] Though at first it seemed that this preparation might be ideal since the free acid would be




128 127 129

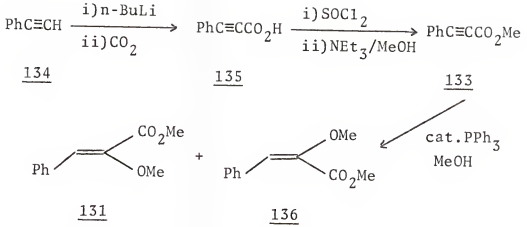
amenable to resolution, the presence of the geminal dihalide function renders that portion of the molecule extremely reactive toward reduction upon reaction with the Fp anion.[42]

A method similar to Ando's was used in the attempted preparation of the α-methoxy ester 130, i.e., a carbene addition to an alkene. The vinyl ester 131 was used as the alkene, while the carbene precursor was phenyldiazomethane 132. Compound 131 was prepared by two

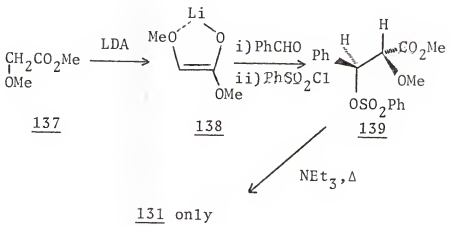



130 131 132

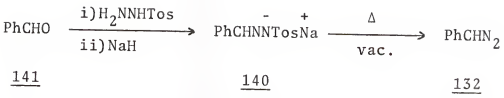
literature methods. Wilson and Tebby used methyl phenylpropiolate in a triphenylphosphine catalyzed methanolysis of the triple bond.[43] The alkyne ester 133 used in Wilson and Tebby's procedure was conveniently prepared in this laboratory by the method outlined.




Though the product is reported to be the pure Z-isomer 131, in our hands both Z-isomer 131 and E-isomer 136 were obtained. The method that gave pure Z-isomer 131 was that of Wenkert et al. employing methyl methoxyacetate 137 in the manner shown.[44]

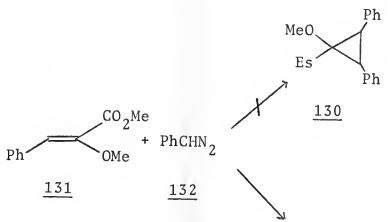



Phenyldiazomethane 132 was prepared by the vacuum pyrolysis of the sodium salt of benzaldehyde tosylhydrazone 140 according to the method of Shecter, et al.[45] However, upon

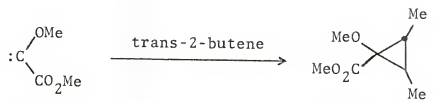



141 140 132

addition of 132 to a THF solution of 131 at reflux temperature, no cycloaddition product was observed after 24 hours. The vinyl ester 131 was recovered along with the azine 142.

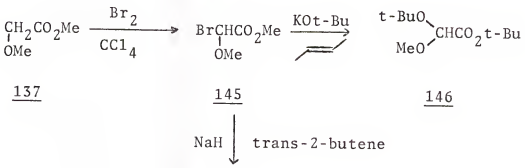


Another obvious choice in the preparation of 126 is the addition of the novel carbene 143 across the double bond of trans-2-butene 144; however, the carbene 143 is unknown at this time. Methyl methoxyacetate 137 appeared




143 126-Me Ester

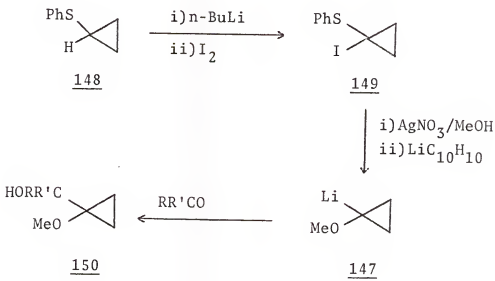
to be a logical precursor to the methoxycarbomethoxycarbene 143 in that bromination and a subsequent base induced α-elimination of 145 might yield the desired carbene 143. Methyl methoxyacetate was brominated to give 145 in quantitative yield; however, treatment of 145 with potassium t-butoxide in neat trans-2-butene yielded only 146 while treatment with NaH in trans-2-butene resulted in no reaction. It appears that the α-carbon of 145 is extremely reactive




137 145 146

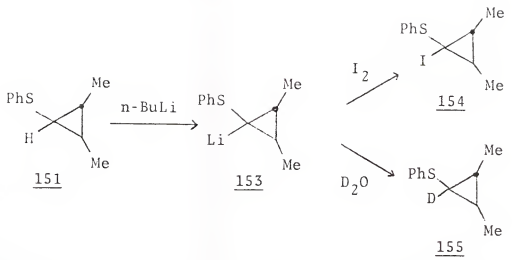
to substitution (colorless 145 fumes upon exposure to moist air) yet the α-hydrogen is not sufficiently acidic to be abstracted by base.

In the recent literature, Cohen et al. have shown that α-methoxylithiocyclopropane 147 reacts with electrophiles such as aldehydes and ketones to yield alcohols.[46]

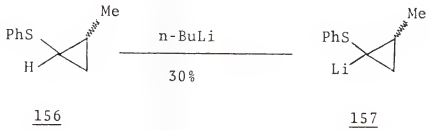



148 149 147 150

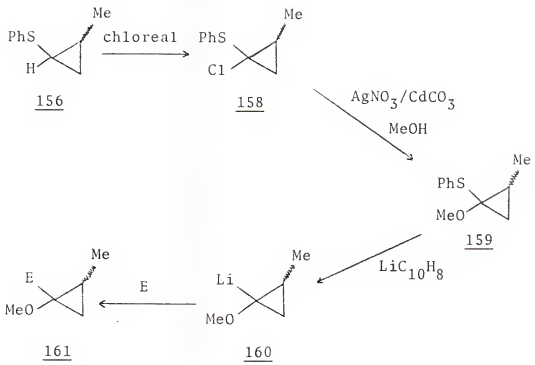
As trans-2,3-dimethylthiophenylcyclopropane 151 was readily available from the carbene addition of ϕSCH to trans-2-butene according to the method of Boche and Schneider, attempts were made to prepare the trans-2,3-dimethyl analogue of 147.[47] Treatment of 151 with one equivalent of n-BuLi failed to generate the desired α-lithiothiophenylcyclopropane 153 as shown by failure of iodination to give 154 or deuteration to give 155.



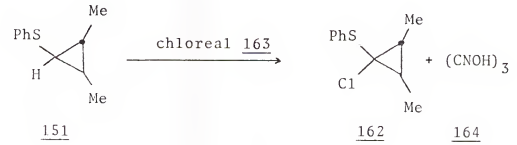

Indeed, Trost has shown reaction of the less-hindered 156 with alkyllithiums results in only 30% exchange to lithiocyclopropane 157; however, an alternative



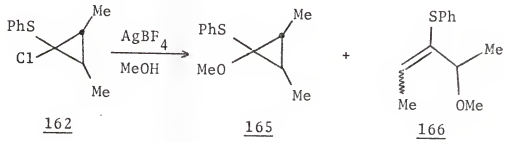

route was devised by Cohen et al. for the 2-methylcyclopropanes, as illustrated below.[48]




Extending the method of Cohen et al. to 126 brought about several intersting results. The preparation of 162 was essentially quantitative from the 2,3-dimethylthiophenylcyclopropane 151 using the recently introduced reagent, chloreal 163 (trichloroisocyanuric acid).



The α-chlorothiophenylcyclopropane 162, previously prepared by Oae et al. using N-chlorosuccinimide, was isolated rather than being transformed to the mixed ketal 165 in situ (according to the method of Cohen et al.[48]).[49] Reaction of 162 with $AgBF_4$ in MeOH at several temperatures resulted in the isolation of 165 and 166: the ratio depending upon reaction temperature as shown in Table 2.

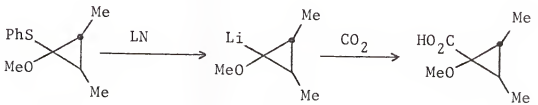



162 165 166

Table 2. Temperature vs. Ratio of 165:166

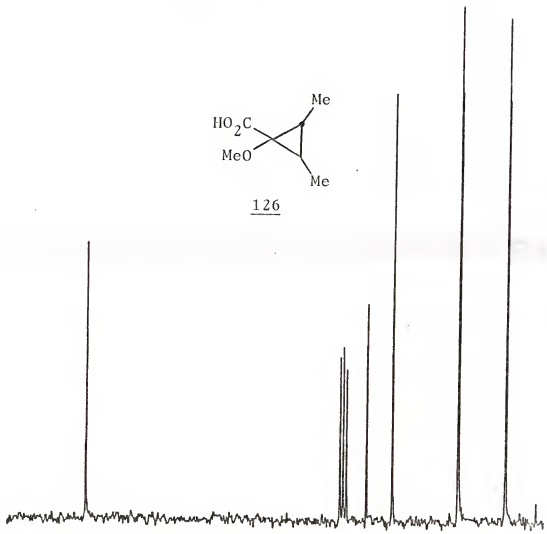
| Temperature (°C) | 165:166 |
|---|---|
| -10 | 4 |
| 0 | 4 |
| 23 | 3 |
| 42 | 2 |

It appeared that at 0°C or below, the optimum ratio of 4:1 (165:166) was obtained. Ring-opening of the intermediate thiophenyl-stabilized cyclopropyl cation was a problem only in that ring-opened 166 had to be removed before reduction with lithium naphthalenide (LN). Low pressure flash chromatography according to the method of Still et al. resulted in isolation of analytically pure 165.[50] The reduction of 159 with LN at -78°C gave only a 55% yield of the alcohol: this is to be contrasted with the 83% isolated yiled of 126, the $^{13}C$ NMR of which is shown in Figure 12.




165 167 126

Inadvertently, the solution of 167 was allowed to warm to -20°C, at which temperature the green-black color of the lithium naphthalenide disappeared leaving the solution orange-red in color. The lithiocyclopropane 167 appears to be quite stable at this temperature, which is not surprising as Trost et al. reported the alkyllithium

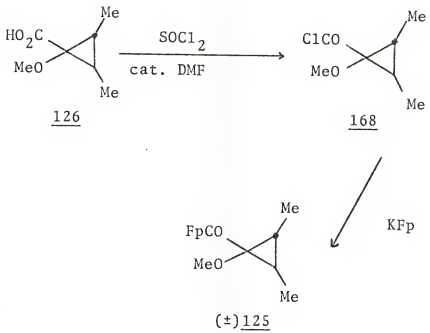



126

| # | ppm |
|---|---|
| 1 | 11.994 |
| 2 | 12.189 |
| 3 | 30.899 |
| 4 | 31.191 |
| 5 | 57.507 |
| 6 | 67.643 |
| 7 | 75.733 |
| 8 | 77.000 |
| 9 | 78.267 |
| 10 | 179.046 |

Figure 12. 25 MHz $^{13}C$ NMR Spectrum of Compound 126.

exchange reactions of 148, the parent thiophenylcyclopropane, at 0°C. The acid chloride 168 was prepared by the DMF catalyzed reaction of 126 with thionyl chloride. Reaction of KFp, prepared by the method of Gladysz et al., with the acid chloride gave acyl complex 125, the 300 MHz $^1$H NMR of which is shown on the following page.[51]




126 168 (±)125

Photolytic decarbonylations of acyl complexes to give the corresponding alkyl complexes are well documented.[52] Moreover, recently several photolytic decarbonylations of cyclopropyl acyl complexes of iron have been reported by this laboratory.[40]

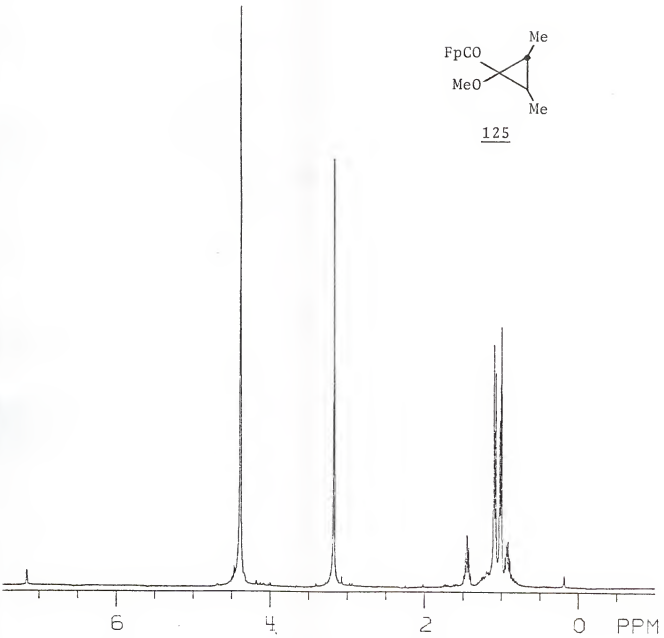
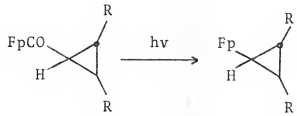
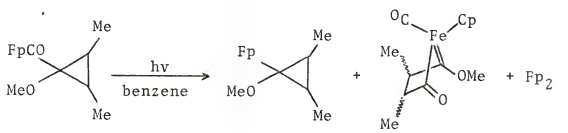



Figure 13. 300 MHz $^{1}H$ NMR Spectrum of Compound 125.




169 170

However, photolysis of 125 under similar conditions led to an extremely low yield of sigma complex (<5%), with the major products being Fp dimer 171 and 172 a red crystalline solid which will be discussed in depth later. As photolysis did not appear to be a viable route to sigma




125 122 172 171

complex 122, alternative methods were then explored. Alexander and Kuhlman report that 173 is stoichiometrically decarbonylated by 174 to give the alkyl complex 175 in 49% yield and the rhodium complex 176.[53]

$$\underset{\underline{173}}{FpCOR} + \underset{\underline{174}}{L_4Rh_2Cl_2} \xrightarrow{CH_3CN} \underset{\underline{175}}{FpR} + \underset{\underline{176}}{RhL_2(CO)Cl}$$

R:p-$MeOC_6H_4$ L:$PPh_3$

The rhodium dimer 174 was conveniently prepared according to the method described in Alexander and Kuhlman's account.

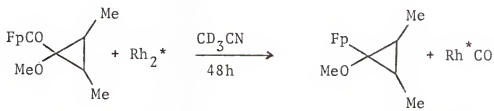
$$2\ \underset{\underline{177}}{RhL_3Cl} \xrightarrow{\text{2-butanone}} \underset{\underline{174}}{L_4Rh_2Cl_2} + \underset{\underline{178}}{2L}$$

L:$PPh_3$

Compound 174 is extremely oxygen-sensitive, quantitatively absorbing one equivalent of oxygen even in the solid state, and therefore all manipulations were performed under rigorous exclusion of oxygen.

The reaction of acyl complex 125 with the rhodium dimer 174 was monitored by 100 MHz $^1H$ NMR in acetonitrile-$d_3$

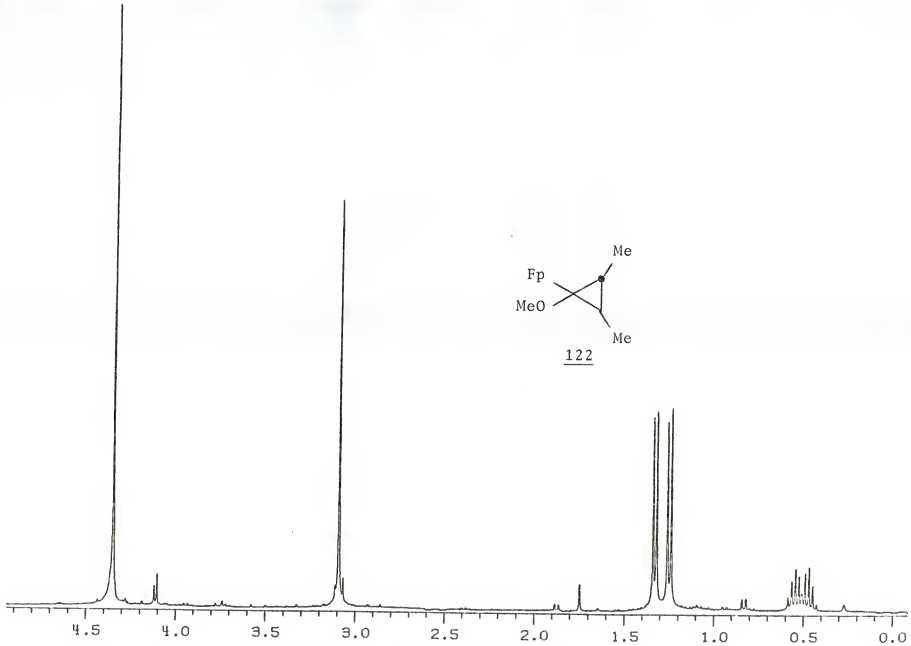
over a 48 hour period. The reaction was conveniently




125 174 122 176

$Rh^{*}$: $(PPh_3)_2RhCl$

followed by the disappearance of the Cp and OMe resonances of 125 with the concomitant appearance of the Cp and OMe resonances due to sigma complex 122. Indeed, the decarbonylation appears to be essentially quantitative by $^1H$ NMR; however, work-up difficulties due to the insolubility of Rh*CO 176 resulted in a certain degree of loss of 122. The sigma complex 122 was isolated in 60% yield as a yellow oil which appeared to be quite volatile. The 300 MHz $^1H$ NMR of 122 is shown in Figure 14. In contrast to the acyl complex 125, the cyclopropyl hydrogens of 122 appear upfield at 0.5 ppm as two overlapping pentets (d of q), typical of cyclopropyl sigma complexes. The correlation of $^1H$ NMR shift values to individual methyl and cyclopropyl hydrogens

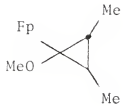



122

Figure 14. 300 MHz $^{1}H$ NMR Spectrum of Compound 122.

presented an interesting challenge. From selective decoupling, it was determined that the lower field doublet ($CH_3$) was coupled to the lower field pentet (CH) while the higher field doublet ($CH_3$) was coupled to the higher field pentet (CH).

As all couplings were on the order of 6.0-6.5 Hz, it was felt that the trans 2,3-dimethyl arrangement had been maintained. The problem of determining which methyl group (or hydrogen) was endo to the methoxy group or the Fp moiety was somewhat more challenging. It was felt, from examination of molecular models, that there was a possibility of observing a Nuclear Overhauser effect (NOE) between the Cp or OMe group and their respective syn-methyl and syn-hydrogen.[54] Using the inversion recovery method for determination of $T_1$ relaxation times, as shown on Figure 15, it was interesting to note that with respect to $^1H$ relaxation rates: $CH_3>CH>OCH_3>>C_5H_5$.[55] Indeed, the $T_1$ for the cyclopentadienyl moiety was on the order of 10-11 sec., thus limiting the pulse interval to 50-55 sec ($T_1$x5.0) during the NOE determination. The NOE experiments were successful in that a 1% enhancement was observed in the intensity of the lower field doublet ($CH_3$) and higher field pentet (CH) upon irradiation of the OMe group. Unfortunately, Block-Sigrid effects prohibited the use of higher energy Rf pulses for a greater NOE enhancement. With the above information, one then




122

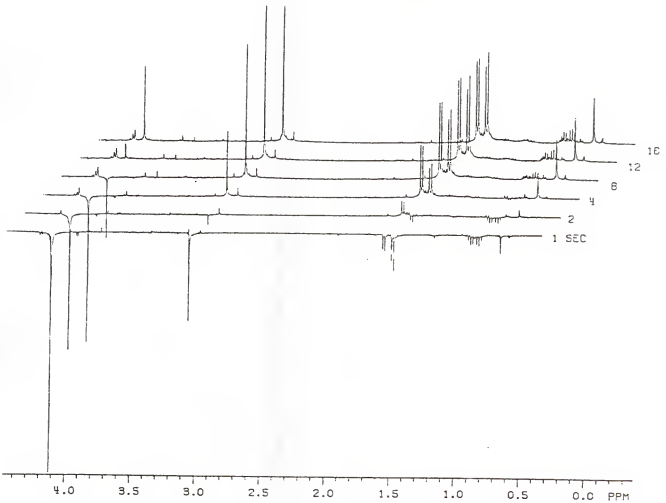
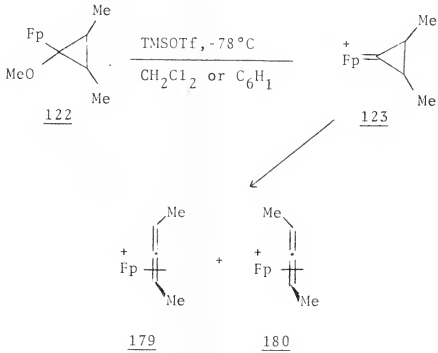



Figure 15. 300 MHz $^{1}H$ NMR Spectrum of Compound 122 Using the Spin Inversion Recovery Method for $T_1$ Determination.

can conclude that the stereochemistry and shift correlation is that shown in Figure 14 for the cyclopropyl sigma complex 122.

The generation of cyclopropylidene complex 123 was accomplished by the TMSOTF induced α-methoxy elimination of the sigma complex 122; however, at -78°C in both $CH_2Cl_2$ or neat cyclohexene, the carbene complex 123 was not observed but rather a mixture of allene complexes 179/180. The 300 MHz $^1H$ NMR is shown in Figure 16. It is interesting to note




122 123 179 180

that the mixture of 179 and 180 is essentially in the same 3:1 ratio observed by Rosenblum et al. from the reaction of 181 with 1,3-dimethylallene 182; although the spectrum of the

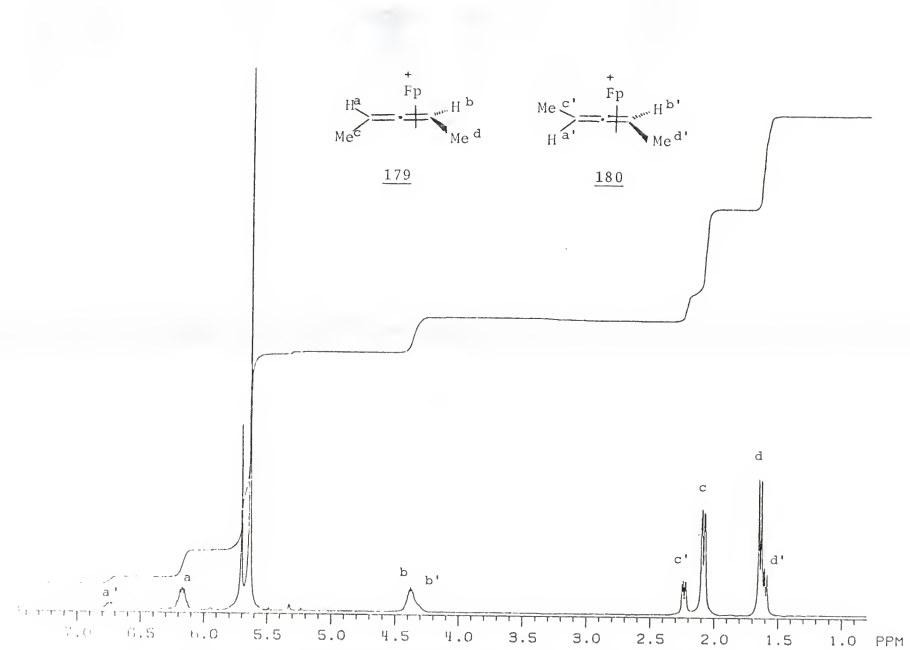
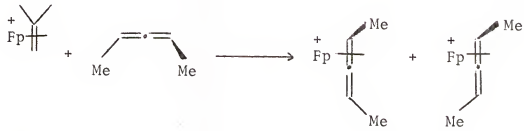



Figure 16. 300 MHz $^{1}H$ NMR Spectrum of an Equilibrium Mixture of Compounds 179 and 180.

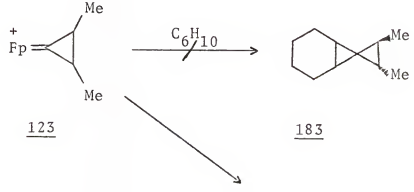
substitution products 179 and 180 were misinterpreted as




181 182 179 180

the vinyl hydrogen on the Fp-substituted carbon appear at the same δ value as the solvent ($CD_3NO_2$) that Rosenblum et al. used.[56]

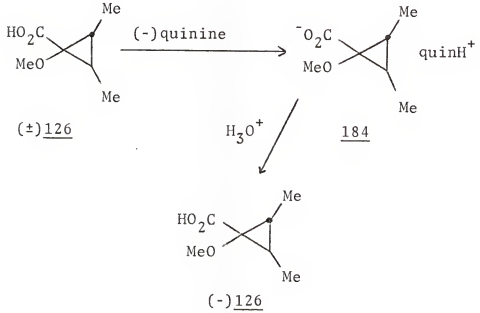
Surprisingly, the generation of carbene complex 123 in neat cyclohexene gave the allene complex only, with no evidence of the cyclohexene adduct 183. Evidently, the rearrangement of carbene complex 123 to allene complexes 179 and 180 is extremely facile even at -78°C.




123 183

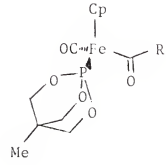
179 + 180 only

To probe the mechanism of ring-opening, the sigma complex 122 was prepared in optically active form. Indeed, the acid 126 was resolved using (-)quinine to generate a pair of diastereomeric salts, the less soluble of which gave use to the acid having $[\alpha]_D^{25} = -17.46^{o}$.

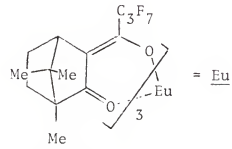



The (-) enriched salt 184 was converted smoothly to the acid, acid chloride 168 and then the acyl complex 125 as previously shown for racemic acyl complex 125. To determine the optical purity of the (-) enriched acyl complex 125, the use of lanthanide shift reagents was explored.

In general, introduction of lanthanide shift reagents to a solution containing a compound with non-bonding electrons results in large changes in $^{1}H$ (or $^{13}C$) chemical shift value compared to the pure compound.[57] If the lanthanide shift reagent is optically active, then its addition to a solution of racemic compound can give different shift values for previously magnetically equivalent hydrogens (or carbons), that is, the complexation of the LSR to each enantiomer of the racemate results in the generation of diastereomeric complexes. This approach has been used by Flood et al. to determine the optical purity of 185 using europium shift reagents i.e. (-)Eu(hfc)$_3$, 186.[58]

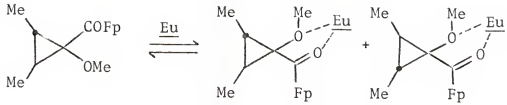



185




(-)Eu(hfc)$_3$ 186

As applied to our system, the $^{1}H$ chemical shifts of 187 and 188 would hopefully be different as they are diastereomeric complexes.




(±)125 187 188

Indeed, as shown in Figure 17, addition of 5% molar equivalent of Eu to racemic acyl complex 125 results in distinct chemical shift differences for the original cyclopentadienyl and methoxy singlets along with noticeable changes in the cyclopropyl region of the spectrum. When a 5% molar equivalent of Eu was added to a solution of the acyl complex 125 made from (-) enriched acid 126, the optical purity appeared to be greater than 95%(Figure 18).

The decarbonylation of optically active 125 was carried out with rhodium complex 174 and the resulting sigma complex was treated with TMSOTF at -78°C thus generating the allene complexes 179 and 180. The allene complexes 179 and 180 showed no rotation ($[\alpha]_D^{25}<0.200$). Further attempts to confirm the optical purity of the allene complex using chiral shift reagents failed. However, as a model it is known that 189

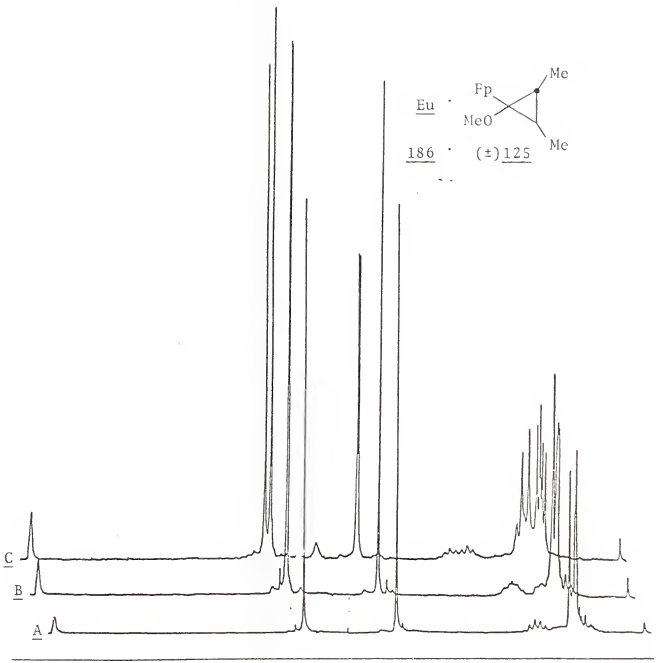



Figure 17. 100 MHz $^{1}H$ NMR Spectrum of: A-Compound 125; B-Compound 125 with 1.0 Mole % 186; C-Compound 125 with 5.0 Mole % 186.

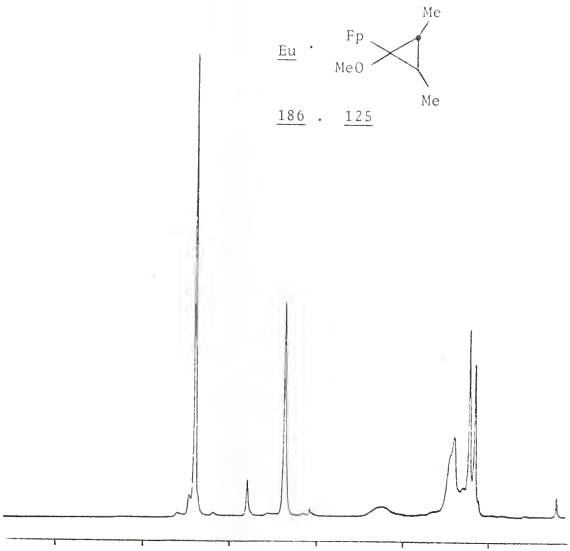
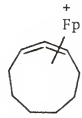



Figure 18. 100 MHz $^{1}H$ NMR Spectrum of Compound 125 [prepared from (-)126] with 5.0 Mole % 186.

has $[\alpha]_D = 22^\circ$, i.e. complexation to the transition metal fragment results in a negligible change in specific rotation. As optically pure 2,3-pentadiene must have a specific rotation greater than 174°, we would expect its complex to have a substantial rotation.[59]




189

190

From the above, one must presume that allene complexes 179 and 180 are racemic, which would be expected if ring opening occurred either through an achiral intermediate such as 74 or if there were no preferential rotation during a concerted opening. The latter seems unlikely since opening of non-complexed cyclopropylidene gives allenes with substantial optical rotations. Though steric effects that would influence concerted opening of the complex would certainly be expected to be different from those in the free carbene, it would require that steric effects favoring rotation in one direction be exactly cancelled by opposing forces, i.e. methyl bumping into beta-hydrogen equal to methyl bumping into Fp. Furthermore, EHMO calculations predict 64, 69, and 65 to have the following relative energies, as shown in Figure 19.[24]

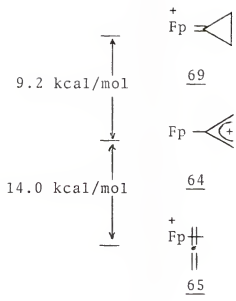
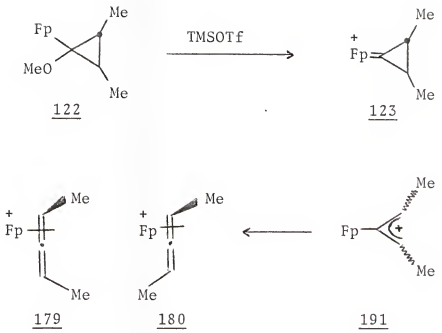



Figure 19. Valence Isomer Energy Differences Using EHMO Calculations for 64, 65, 69 (Courtesy of W.R. Winchester).

Insofar as this ordering is reliable, this precludes a significant activation barrier for conversion of 69 to 64.

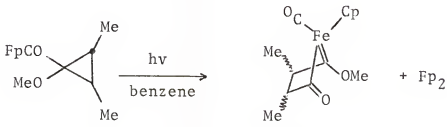
From these considerations, we suggest as the most likely mechanism for conversion of 122 to 179 and 180 a symmetry allowed disrotatory opening of 123 to 191 (presumably, but not necessarily, from a preferred upright conformation) followed by collapse to the allene complexes 179 and 180.




122 123 179 180 191

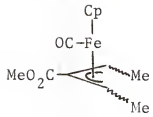
This is in contrast to the opening of non-complexed cyclopropylidenes which are believed to begin by the same disrotatory mode but, before reaching a planar dipole (which may be at quite high energy), flip back in a conrotatory fashion to give the perpendicular allene.[60]

As mentioned previously, attempts to prepare 122 by photolysis of acyl complex 125 gave unexpected results, i.e. isolation of the novel carbene complex 172 presumably via the desired sigma complex 122. In early experiments, photolyses of acyl complex 125 were performed in acetone-$d_6$. Under these conditions, monitoring the reaction progress (e.g. following the loss of acyl Cp resonance and concomitant growth of sigma Cp resonance) was somewhat confusing in that several resonances in the Cp region appeared during photolysis. However, photolysis in benzene resulted in the appearance of only two new Cp resonances, which were shown to be the novel carbene complex 172 and Fp dimer 171.




125 172 171

When the red compound to which structure 172 was ultimately assigned was initially isolated, it was not possible using 100 MHz $^1$H NMR, IR, and mass spectrum to unambiguously distinguish it from its isomer 192. Complexes such as 192 are known and the $^1$H chemical shifts are consistent with those observed for the new red solid.[61]




192

It was felt that at higher field (i.e. 300 MHz) one could distinguish between 172 and 192 as the vinyl hydrogens in 192 would each be a quartet while the ring hydrogens in 172 would be, at the very least, a pentet. Indeed, the 300 MHz $^{1}H$ NMR, as shown in Figure 20, showed two pentets at 1.93 and 2.11 ppm, clearly obviating structure 192.

Though 172 was then the most reasonable structure for the red crystalline solid, it was the 75 MHz $^{13}C$ NMR that provided definitive evidence for the proposed structure, as shown in Figure 21. Perhaps most indicative of structure 172 is the extreme downfield resonance at 348 ppm which is typical of carbene carbons, and the resonance at 270 ppm which is typical of acyl carbonyl carbons.

Prior to isolation of 172, the only carbene complex similar to 172 was that isolated by Rosenblum upon treatment of cyclohexene oxide 193 with KFp followed by methylation of the equilibrium mixture of 194 and 195 to give 196 and 197.

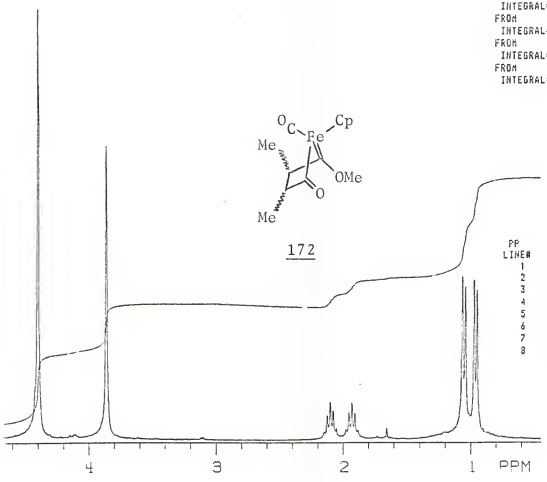
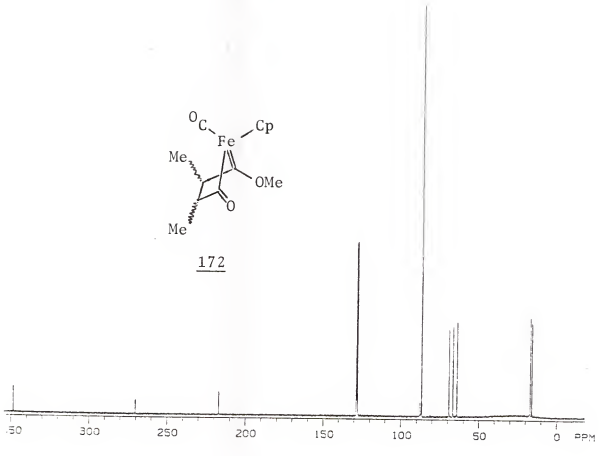
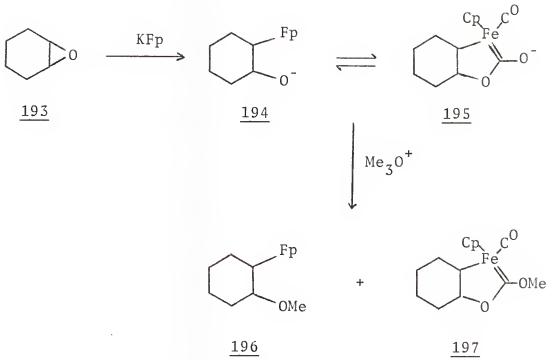



Figure 20. 300 MHz $^{1}$H NMR Spectrum of Compound 172.




172

Figure 21. 75 MHz $^{13}C$ NMR Spectrum of Compound 172.



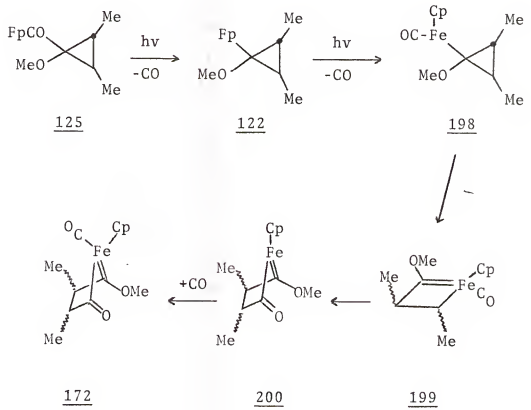

193 194 195

196 197

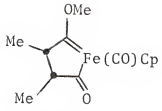
The carbene carbon resonance of 197 is at 266 ppm, much further upfield than in 172, due to the shielding afforded by an additional alkoxy fragment.[62]

A reasonable mechanism for formation of 172 from 125 is outlined below. As expected from this mechanism, photolysis of sigma complex 122 under conditions similar to that for photolysis of acyl complex 125 did indeed give the carbene complex 172, albeit at a somewhat lower yield presumably due to the lower concentration of CO. Furthermore, when sigma complex 122 was photolyzed under 5.0 atm CO, the rearrangement was completely suppressed. This is consistent

with a mechanism that requires a vacant coordination site (e.g. 198 and 200) as shown in the proposed mechanism.




In principle, rearrangement of 122 to 172 would give four different diastereomers: 201 - 204. In fact, the 100 MHz $^{1}H$ NMR of the crude reaction mixture shows a large preponderance of only one stereoisomer with, at most, traces of two minor products, possibly isomers. However, as the

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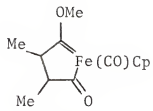


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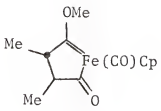


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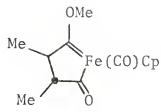
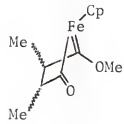



204

presumed minor products were never completely characterized (i.e. only 100 MHz $^{1}$H NMR) their identity remains speculative, at best.

The isolation of a single isomer suggest a reaction that is at least highly stereoselective and possibly stereospecific. Although this assumption cannot be secure until the cis isomer is prepared, the formation of a single stereoisomer also requires a highly regioselective rearrangement or equilibration at iron which would interconvert two stereoisomers without affecting the trans relationship of the two methyls.

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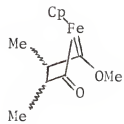
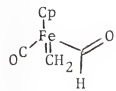



205

Although both diastereomeric and conformational stereochemistry of 172 must await an x-ray, it is noteworthy that EHMO calculations of the model system 206 predict confomation 201 (which correspondsto Hoffmann's preferred upright conformation for $Fp{=}CH_2^+$) to be favored over 208 by 11.7 kcal/mole.[63] This is pertinent because conformation 207 corresponds to 172 while 208 corresponds to the higher energy bis-bisecting geometry 209. Furthermore, an observed NOE between Cp and OMe and the absence of such an effect between Cp and either methyl is as expected for conformation 172, though not strictly demanded by it.

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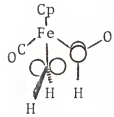

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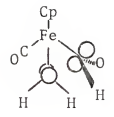

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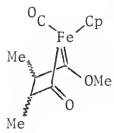
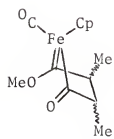


172

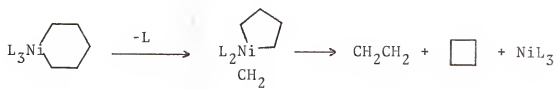


209

The facility of the rearrangement of 122 to 172 is striking and probably results from a combination of methoxy acceleration and relief of strain. Thus, the methoxy must favor this reaction since its position on saturated carbon can do little to stabilize 122 while conjugation with the p-orbital in the carbene should have a significant impact on its energy. It is more difficult to assess the contribution of strain relief to this reaction because even though

there would be little question that ring strain on the cyclopropane side of the equilibrium is about 25 kcal/mole, the strain on the metallocyclobutene side is not known.[64] Were the rearrangement to a carbocycle, strain would slightly favor the cyclopropane; however, small ring metallocycles are probably much less strained than their carbocyclic analogues.[65] However, it should be pointed out that if relief of ring strain is important, it is unlikely that, alone, it is sufficient to induce the rearrangement since photolysis of cyclopropyl sigma complexes with α-hydrogens showed no tendency to rearrange.

The significance of the rearrangement of 122 to 172 lies in the fact that there has been, to date, only one other case to our knowledge of such a rearrangement. Grubbs et al. postulated the intermediacy of 210 based on product labeling studies in the thermolysis of 211.[66] Though Hoffmann and

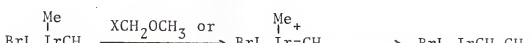



211 210 212 213 214

coworkers have predicted that the interconversion of 215 and 216 should be quite facile, it appears that the majority of cases involve solely the transformation of 215 to 216.[67,68]

215 216

Thorn and Tulip isolated 217 from the electrophile induced rearrangement of 218, presumably via the alkylcarbene 219.[69]



218 219 217

L:$PMe_3$ X:halogen

Cooper and Green have suggested that the reason rearrangements from saturated carbon to metal to give carbene complexes have not been more frequently encountered may be thermodynamic in origin.[70]

It appears, then, that the aforementioned combination of methoxy stabilization and probable relief of ring strain

in going from 122 to 172 is sufficient to reverse the more common thermodynamic preference of 215 to 216.

# CHAPTER III
# EXPERIMENTAL

Benzene, diethyl ether, hexane, and tetrahydrofuran were distilled from sodium benzophenone ketyl. Methylene chloride was distilled from $P_2O_5$ after 24 h reflux. Silica gel was either Baker 60-200 mesh or M.C.B. 230-400 mesh (the latter used for low-pressure chromatography according to the method of Still et al.[50]). Alumina was Brockman 80-200 mesh activity I which was deactivated to activity II by the addition of 3% (w/w) water. Both silica gel and alumina were degassed overnight (0.25 mm Hg, 25°C) prior to use. NMR spectra were taken on a JEOL PMX-60 (60 MHz), JEOL FX-100 (100 MHz), or a Nicolet NC-300 (300 MHz). Infrared data were recorded on a Perkin-Elmer 137 spectrophotomer. Atlantic Microlab, Inc. performed C, H analyses. Melting points (uncorrected) were obtained using a Thomas-Hoover apparatus. All solutions containing transition metals or organolithium reagents, as well as any resulting solids, were manipulated under inert atmosphere (Schlenk tube or glove box) conditions.

Preparation of Tropone (85). This compound was prepared by a modified procedure of Radlich from cycloheptatriene. Instead of allowing the reaction mixture to stand overnight, it was stirred with a mechanical stirrer in a Morton flask. This improved the yield to 37% (lit 25%).[71]

Preparation of 1-,2-, and 3-Bromocycloheptatrienes (36). This isomeric mixture was prepared from bromotropylium bromide according to the method of Fohlisch and Haug.[72]

Preparation of 1,3,5-Cycloheptatrien-1-carboxylic acid chloride (76). This compound was surreptitiously obtained from W. R. Winchester according to the method of Murph the Surf.[73]

Preparation of 4,5-Benzotropone (87). This compound was prepared by the method of Paquette and Ewing.[28]

Preparation of 1,2-Benzo-5-bromocycloheptatriene (90). This material was prepared from 1,2-benzo-5-bromotropylium bromide according to the method of Fohlisch with the modification reported by Allison.[29]

Preparation of 1,2-dihydronaphthalene (97). This compound was prepared according to the method of Waali as reported by Allison.[30]

Preparation of 1,2-Benzo-4- and 1,2-Benzo-6-bromocycloheptatrienes (99). This compound was prepared by the method of Allison.[30]

Preparation of Dodecacarbonyltriruthenium (83). This compound was either prepared by the method of Dawes and Holmes, or purchased from Strem. Chem.[74]

Preparation of Bromodicarbonyl-$\eta^5$-cyclopentadienylruthenium (81). This compound was prepared by the method of Eisenstadt, Tannenbaum, and Efraty.[26]

Preparation of carbonylchloro-$\eta^5$-cyclopentadienyltributylphosphineruthenium (102). Dodecacarbonyltriruthenium (100g, 1.56 mmol) and freshly prepared cyclopentadiene (4.0 mL, 49 mmol) in 150 mL heptane were refluxed for 3.0 hours, doing which time the initially orange solution became burgundy, then orange, and finally pale yellow. The yellow solution was cooled to 80°C and tri-n-butylphosphine (0.947g, 4.68 mmol) was added. Gas evolution was immediate; however, the solution was allowed to stir for 20 minutes at 80°C, by which time gas evolution had ceased. Solvent was removed in vacuo leaving an orange-brown oil which was dissolved in 125 mL $CHCl_3$, and stirred overnight at room temperature. Silica gel (5.0g, 60-200 mesh) was added to the solution and solvent was removed in vacuo. The resulting yellow solid was placed on a 1"x 12" silica gel column (230-400 mesh) and eluted initially with 100 mL pentane to remove residual tri-n-butylphosphine. Elution with ethyl acetate-pentane (1:9 v/v) resulted in collection of an orange band. Solvent was removed in vacuo and the yellow crystalline product was dissolved in 10 mL $CH_2Cl_2$, to which were added 40 mL

hexane. Upon removal of approximately two-thirds of the solvent in vacuo and brief cooling to -78°C, yellow crystals separated out. The crystals were filtered, washed with pentane (3x10 mL), and briefly dried under vacuum (0.200 torr, 25°C) resulting in 1.26g (62%) of 102; mp 99-100°C; IR (hexane) $\nu_{CO}$ 1900 $cm^{-1}$ (vs); $^1H$ NMR (60 MHz, $CDCl_3$) δ1.0-2.3 (m,27H), 5.3 (s,5h); $^{13}C$ NMR (25 MHz, $CDCl_3$) δ13.62 ($C_4$), 24.09 ($C_2$, $^2J_{PC}$=13.41 Hz) 25.67 ($C_3$, $^3J_{PC}$=1.04 Hz), 27.65 ($C_1$, $^1J_{PC}$=28.67 Hz), 88.85 (Cp), 203.70 (C≡O, $^2J_{PC}$=20.65 Hz); mass spectrum, m/e 432 ($M^+$), 404 ($M^+$-CO), 366 ($M^+$-$C_5H_6$); Anal Calcd for $C_{18}H_{32}OClPRu$: C,50.05; H, 7.47. Found: C, 50.21; H, 7.48.

Preparation of Dicarbonyl(1,3,5-cycloheptatrien-1-carbonyl)-$\eta^5$-cyclopentadienylruthenium (79). Bromodicarbonyl-$\eta^5$-cyclopentadienylruthenium (81) (0.500g, 1.65 mmol) was added as a yellow solid to a stirred sodium amalgam (0.250g Na, 10.9 mmol; 101.25g Hg, 0.505 mol) in 15 mL THF at room temperature. The yellow solid gave rise to a green suspension immediately, which was allowed to stir for six hours at room temperature. The green suspension had become orange-red by this time and was separated from residual sodium amalgam via cannula into another Schlenk tube and cooled to -78°C with stirring. To the solution of sodium dicarbonyl-$\eta^5$-cyclopentadienylruthenate at -78°C was added 1,3,5-cycloheptatrien-1-carbonyl chloride (0.256g, 1.65 mmol) in 10 mL THF. The stirred solution was then allowed to warm to room temperature and

stir over a 12 hour period. Solvent was removed in vacuo and the viscous orange-brown oil was extracted with benzene (3x30 mL). After filtration of the benzene extracts through a Celite mat (∿20g) on a coarse, sintered-glass frit, silica gel (1.0g, 60-200 mesh) was added and solvent was removed in vacuo. The resulting orange solid was then placed on a 1"x 9" silica gel column (230-400 mesh) and eluted with ethyl acetate-pentane (15% v/v) at 2 in/min. A yellow band was collected which upon removal of solvent in vacuo proved to be a viscous orange oil. After storage under vacuum (0.100 torr, 25°C, 12 hr), the oil crystallized to give 0.364g (64%) yellow crystals (79): mp IR ($CDCl_3$)$\nu_{CO}$ 2020 $cm^{-1}$ (vs), 1940 $cm^{-1}$ (vs), 1800 $cm^{-1}$ (w); $^1H$ NMR (100 MHz, $CDCl_3$) δ2.4 (d, 2H, $^3J_{HH}$=7.1 Hz), 5.3 (s,5H), 5.3-5.4 (m,1H), 5.5-5.6 (m,1H), 6.7-6.8 (m, 3H); $^{13}C$ NMR (25 MHz, $CDCl_3$)δ27.44 ($C_7$), 88.84 ($C_p$), 124.46, 126.61, 128.70, 132.79, 133.29 ($C_{2-6}$), 144.88 ($C_1$), 199.37 (C≡O), 235.87 (C=O); mass spectrum, m/e 342 ($M^+$), 314 ($M^+$-CO), 286 ($M^+$-2CO), 91 ($C_7H_7$). Anal. Calcd. for $C_{15}H_{12}O_3Ru$: C, 52.78, H, 3.54. Found: C, 52.64; H, 3.57.

Preparation of Dicarbonyl(1,3,5-cycloheptatrien-1-yl)-$\eta^5$-cyclopentadienylruthenium (80). A mixture of 1-,2-, and 3-bromocycloheptatrienes (0.570g, 3.31 mmol) was dissolved in THF (10 mL) and cooled to -78°C with stirring. Buthyllithium (2.21 mL 1.5 M solution in hexane) was added dropwise slowly, resulting in formation of the green-black color of the cycloheptatrienyllithiums. The solution was allowed to stir for 30 min at -78°C. Bromodicarbonyl-$\eta^5$-cyclopentadienylruthenium (81) (1.00g, 3.31 mmol) was dissolved in THF (10 mL), cooled to -78°C, and then added slowly to the cold (-78°C) cycloheptatrienyllithium solution. The reaction vessel was allowed to warm to room temperature slowly and then stir for an additional 30 min. Silica gel (2.0g, 60-200 mesh) was added to the solution and solvent removed in vacuo. The resulting orange solid was placed on a 1"x 9" silica gel column (230-400 mesh) and eluted at 2.0 in/min with ethyl acetate-pentane (5% v/v). A yellow band was collected and, upon removal of solvent in vacuo, 0.390g (38%) air-sensitive orange oil ( was obtained: IR(neat) $\nu_{CO}$ 2015(s), 1970(vs)$cm^{-1}$; $^1H$ NMR (100 MHz, $CDCl_3$) $\delta$ 2.10 (t,2H, $^3J_{HH}$=6.7 Hz), 2.60 (d,2H, $^3J_{HH}$=6.5 Hz), 5.10 (s,5H), 5.20 (s,5H), 4.8-5.6 (m,2H each isomer), 5.8-6.8 (m,3H each isomer); $^{13}C$ NMR (25 MHz, $CDCl_3$) $\delta$ 49.03 ($C_7$), 87.18 (Cp), 116.28, 125.39, 125.83, 132.07, 137.33, 141.52 ($C_1$-$C_6$), 200.29 (C≡O): other isomer $\delta$ 27.73 ($C_7$), 88.50 (Cp), 113.60, 118.52, 126.85, 135.67, 141.18, 141.33 ($C_1$-$C_6$),

200.63 (C≡O): mass spectrum, m/e 314 ($M^+$), 286 ($M^+$-CO), 258 ($M^+$-2CO). Anal. Calcd. for $C_{14}H_{12}O_2Ru$: C, 53.67, H, 3.86. Found: C, 53.48; H, 3.91.

Preparation of Dicarbonyl-$\eta^1$-cycloheptatrienylidene-$\eta^5$-cyclopentadienylruthenium Hexafluorophosphate (53a). The sigma complex (80) (0.235g, 0.75 mmol) was dissolved in methylene chloride (7.0 mL) and cooled to -78°C with stirring. Triphenylcarbenium hexafluorophosphate (0.291g, 0.75 mmol) was dissolved in methylene chloride, cooled to -78°C, and then added to the cold (-78°C) solution of sigma complex. The solution was allowed to stir for 30 min at -78°C and slowly warm to room temperature with an additional 30 min stirring. Solvent was removed until 2.0-3.0 mL remained, at which time the solution was cooled to -78°C and diethyl ether (20 mL) was added, precipitating a brown solid. Filtration, washing (diethyl ether, 3x15 mL), and subsequent vacuum drying (25°C, 0.200 torr) resulted in 0.220g (64%) air-stable, brown solid (53a): mp °C; IR(CDCl$_3$)$\nu_{CO}$ 2020(s), 1980(vs)cm$^{-1}$: $^1$H NMR (100 MHz, $CD_3NO_2$) δ 5.60 (s,5H), 7.90-8.35 (m,2H), 8.40-8.70 (m,2H), 9.90 (d,2H, $^3J_{HH}$=10.0 Hz); $^{13}$C NMR (25.2 MHz, $CD_3NO_2$) δ 91.15 (Cp), 140.91 ($C_{3,6}$), 149.19 ($C_{4,5}$), 170.05 ($C_{2,7}$), 198.66(C≡O), 223.56 ($C_1$): Anal. Calcd. for $C_{14}H_{11}O_2F_6PRu$: C,36.77; H,2.42. Found: C,36.90; H,2.48.

Preparation of Carbonyl-(1,3,5-cycloheptatrien-1-yl)-$\eta^5$-cyclopentadienyl-tri-n-butylphosphineruthenium (21). A mixture of 1-,2-, and 3-bromocycloheptatrienes (0.55g, 3.24 mmol) was dissolved in 5.0 mL THF and cooled to -78°C with stirring. Butyllithium (2.2 mL 1.5 M solution, 3.30 mmol) was added dropwise slowly resulting in formation of the green-black color of the cycloheptatrienyllithiums. The solution was allowed to stir at -78°C for 30 minutes. Compound 4 (0.70g, 1.62 mmol, 0.50 eq.) was dissolved in THF (15.0 mL), cooled to -78°C, and then added slowly to the cold (-78°C) cycloheptatrienyllithium solution. Stirring was continued for one hour at -78°C and then the solution was allowed to warm to room temperature over a two hour period. Silica gel (4.0g, 60-200 mesh) was added to the solution and solvent removed in vacuo. The resulting red-brown solid was placed on a 1"x 12" low pressure, silica gel column (230-400 mesh) and upon elution with ethyl acetate-pentane (3% v/v), a yellow band was collected. Upon removal of solvent in vacuo, an orange oil was obtained. The oil was rechromatographed as above; however neutral grade II alumina was substituted for both meshes of silica gel. Solvent was removed in vacuo from the yellow band collected with ethyl acetate-pentane (3% v/v) which resulted in 0.200g (25%) orange oil 21: IR(neat)$\nu_{CO}$ 1900 $cm^{-1}$(vs); $^1H$ NMR ($CDCl_3$) $\delta$ 0.70-2.0 (m,27H), 2.4(d,2H,$^3J_{HH}$= 7.0 Hz), 5.0 (s,5H), 5.2(d,1H,$^3J_{HH}$=6.5 Hz), 5.9-6.3(m,4H); $^{13}C$ NMR

($CDCl_3$) δ 13.6(butyl $C_4$), 24.1 (butyl $C_2$,d,$^2J_{PC}$=12.8 Hz), 25.7 (butyl $C_3$,d,$^3J_{PC}$=2.H Hz), 28.8 (butyl $C_1$,d,$^1J_{PC}$=28.7 Hz), 50.2($C_7$), 86.5 (Cp,d,$^3J_{PC}$=1.22 Hz), 116.1, 122.8, 125.3, 132.1, 135.6 ($C_{2-6}$), 155.8 ($C_1$,d,$^2J_{PC}$=10.0 Hz), 201.0 (C≡O, d,$^2J_{PC}$=20.0 Hz); high res. mass spectrum, m/e calcd 488.1782, found 488.1798. Anal. Calcd. for $C_{24}H_{39}OPRu$: C,61.68; H,8.07. Found: C,61.73; H,8.09.

Preparation of Carbonyl-$\eta^1$-cycloheptatrienylidene-$\eta^5$-cyclopentadienyltri-n-butylphosphineruthenium Hexafluorophosphate (53b). The sigma complex (106)(0.100g, 0.205 mmol) was dissolved in 5.0 mL $CH_2Cl_2$ and immediately cooled to -78°C with stirring. Triphenylcarbenium hexafluorophosphate (0.080g, 0.205 mmol) in 5.0 mL $CH_2Cl_2$ at -78°C was then added dropwise to the cold solution of sigma complex 21, which resulted in color change of yellow to red. Stirring was continued at -78°C for 8.0 hours, followed by one hour at room temperature. Solvent was then removed in vacuo until 2-3 mL of solvent remained. Subsequently, the solution was cooled to -78°C and 45 mL diethyl ether were added which resulted in formation of a red precipitate. The suspension was immediately filtered via coarse glass frit and washed with cold diethyl ether (0°C, 2x15 mL). Drying of the red solid (0.200 torr, 25°C) resulted in 0.080g (64%) carbene complex 22; mp 110-111°C (dec); IR($CDCl_3$)$\nu_{CO}$ 2020, 1980 $cm^{-1}$; $^1H$ NMR (60 MHz, $CD_3NO_2$) δ 0.3-1.9 (m,27 H), 5.2 (s,5H), 6.9-7.3 (m,2H), 7.5-7.9 (m,2H), 9.1 (d,2H,$^3J_{HH}$=11.0 Hz);

$^{13}C$ NMR (25 MHz, $CD_3NO_2$) δ 14.0 (butyl $C_4$), 25.0 (butyl $C_2$,d, $^2J_{PC}$=13.4 Hz), 26.8 (butyl $C_3$), 29.6 (butyl $C_1$, d, $^1J_{PC}$=29.3 Hz), 91.4 (Cp), 135.2 ($C_{3,6}$), 145.5 ($C_{4,5}$), 168.1 ($C_{2,7}$), 179.0 (C≡O), 256.2 ($C_1$); Anal. Calcd. for $C_{24}H_{38}OF_6P_2Ru$: C, 47.54; H, 6.06. Found: C, 47.73; H, 5.81.

Preparation of Dicarbonyl(1,2-benzocycloheptatrien-5-yl)-$\eta^5$-cyclopentadienylruthenium (91). 1,2-Benzo-5-bromocycloheptatriene (90) (0.534g, 2.42 mmol) was dissolved in 10 mL THF and cooled to -78°C with stirring. Butyllithium (1.0 mL 2.5 M solution, 2.5 mmol) was added slowly over a three minute period giving a blue-green solution, which was allowed to stir at -78°C for 30 minutes. A cold (-78°C) solution of 3 (0.730g, 2.42 mmol) in 10 mL THF was then added over a 10 minute period and upon completion of addition, the reaction mixture was allowed to stir for 60 minutes at -78°C and 60 minutes at 25°C. Solvent was then removed in vacuo and the residue taken up in benzene (3x10 mL) and filtered through a Celite mat on a coarse, sintered-glass frit. To the filtered solution was added silica gel (5.0g, 60-200 mesh) and the solvent was then removed in vacuo. The solid residue was then placed on a low-pressure, silica gel column (0.75"x9", 230-400 mesh prepared with ethyl acetate-pentane, 1% v/v). Elution with ethyl acetate-pentane (1% v/v) brought down a pale yellow band with the solvent front; collection was begun when the band was two inches from the bottom of the column. Removal of solvent in vacuo and crystallization of the resulting pale yellow from

$CH_2Cl_2$-hexane (as in the preparation of 102) gave 0.120g (14%) pale yellow crystalls (91); mp 105-106°C (dec); IR ($CDCl_3$) 2020(s), 1960(vs)$cm^{-1}$, $^1H$ NMR (100 MHz, $CDCl_3$) δ 2.95 (d,2H, $^3J_{HH}$=6.7 Hz), 5.08 (s,5H), 5.59(t,1H, $^3J_{HH}$=6.7 Hz), 6.59(s,2H), 7.10-7.33(m,4H); $^{13}C$ NMR (25 MHz, $CDCl_3$) δ 39.91 ($C_7$), 88.84 (Cp), 124.13, 124.71, 126.57, 127.39, 127.64, 133.24, 135.92, 137,87, 144.26 (10 vinyl and aromatic carbons), 200.84 (C≡O); mass spectrum, m/e 364($M^+$), 336($M^+$-CO), 308($M^+$-2CO); Anal. Calcd. for $C_{18}H_{14}O_2Ru$: C,59.50; H,3.88. Found: C,59.43; H,3.94.

Preparation of Dicarbonyl-$\eta^1$-4,5-benzocycloheptatrienylidene-$\eta^5$-cyclopentadienylruthenium Hexafluorophosphate (55a). Sigma complex (91)(0.112g, 0.308 mmol) was dissolved in methylene chloride (10 mL) and cooled to -78°C. Triphenylcarbenium hexafluorophosphate (0.120g, 0.308 mmol) was dissolved in methylene chloride (10mL) and cooled to -78°C and then added via cannula to the rapidly stirred solution of sigma complex (91) at -78°C, which darkened immediately from a pale yellow color to a red-brown color. The solution was kept at -78°C for 60 min, then allowed to warm to room temperature, at which time approximately 75% (15 mL) solvent was removed in vacuo. The solution was cooled to -78°C and then cold (<0°C) diethyl ether (50 mL) was added to the solution, thus precipating 55a and the pi-complex impurity 92. The suspension was

rapidly filtered and washed with cold (<0°C) diethyl ether (2x20 mL), then placed under vacuum (0.250 mm Hg, 25°C) for several hours. After drying, 0.141g yellow-brown solid was obtained. From $^1$H NMR (60 MHz), it appeared that 55a and 92 had been formed in 1:1 ratio. Analytical data for 55a: $^1$H NMR (60 MHz, $CD_3NO_2$) δ 5.70 (s,5H), 8.2-8.7 (m,6H), 9.70 (d,2H,$^3J_{HH}$=10.0 Hz); $^{13}$C NMR (300 MHz, $CD_3NO_2$) δ92.074 (Cp), 137.016, 137.612, 138.104, 143.693, 158.866 (vinyl and aromatic carbons), 244.715 (carbene carbon).

Preparation of Dicarbonyl(1,2-benzocycloheptatrien-4-yl)-$\eta^5$-cyclopentadienylruthenium (95). The bromoalkene (99) (0.640g, 2.93 mmol) was dissolved in THF (5 mL) and cooled to -78°C. Butyllithium (2.0 mL 1.50 M, 3.0 mmol) was added dropwise slowly to the bromoalkene solution, which went from colorless to green over the course of butyllithium addition. After stirring at -78°C for 30 min, the ruthenium halide (81)(0.800g, 2.648 mmol, 0.91 eq.) in THF (10 mL) was added to the rapidly stirred alkyllithium solution at -78°C. The solution was allowed to stir at -78°C for 30 min, then allowed to warm to room temperature over a 1 h period. Solvent was removed in vacuo and the residue was dissolved in the minimum amount of ethyl acetate-pentane (10:90 v/v) solution and eluted at 2.0 in/min on a 1"x 12" low pressure column (silica gel, 230-400 mesh, prepared with ethyl acetate-pentane, 10:90 v/v). Collection of the yellow

band and removal of solvent in vacuo gave 0.521g (54%) orange oil (95): IR(neat $\nu_{CO}$ 2018(s) 1973(vs) $cm^{-1}$; $^1H$ NMR (60 MHz,$CDCl_3$) δ2.90 (d,2H,$^3J_{HH}$=7.0 Hz), 5.33(s,5H), 5.40 (m,1H), 6.20(d,1H,$^3J_{HH}$=8.50 Hz), 7.2-7.5 (m,5H);$^{13}C$ NMR (25 MHz,$CDCl_3$) δ34.213($CH_2$), 88.842 (Cp), 118.276, 125.099, 126.171, 126.366, 126.512, 126.610, 137.185, 137.331, 140.547, 142.692 (vinyl and aromatic carbons), 200.733 (C≡O); mass spectrum, m/e 364 ($M^+$). Anal. Calcd. for $C_{18}H_{14}O_2Ru$: C, 59.50; H,3.88. Found: C,59.75; H,3.90.

Preparation of Dicarbonyl-$\eta^1$-(3,4-benzocycloheptatrienyli-dene)-$\eta^5$-cyclopentadienylruthenium Hexafluorophosphate (57a). The sigma complex (95)(0.200g, 0.552 mmol) was dissolved in methylene chloride (5 mL) and cooled to -78°C. Triphenylcarbenium hexafluorophosphate (0.214g, 0.552 mmol) was dissolved in methylene chloride (10 mL) and cooled to -78°C, then added via cannula to the rapidly stirred solution of sigma complex at -78°C. The sigma complex solution darkened from yellow to orange-brown in color during the addition of the trityl salt. The solution was allowed to stir at -78°C for 60 min, then allowed to warm to room temperature over a 60 min period. Solvent (approximately 10 mL) was removed and the solution cooled to -78°C. Cold (<0°C) diethyl ether (50 mL) was added rapidly, thus precipitating carbene complex (57a) and pi-complex (92). The suspension was filtered and

washed with cold (<0°C) diethyl ether (2x20 mL). The resulting solid was then placed under vacuum (0.250 mm Hg, 25°C) for several hours, giving 0.250g yellow-brown solid containing (57a) and (92) in 1:1 ratio. Analytical data for 57a: $^{1}$H NMR ($CD_2Cl_2$, 100 MHz) δ5.849 (s,5H), 8.020-8.460(m,5H), 9.120(d,1H,$^{3}J_{HH}$=10.13 Hz), 9.699(d,1H,$^{3}J_{HH}$=9.60 Hz),10.171(s,1H); $^{13}$C NMR (25 MHz,$CD_3NO_2$)δ91.162(Cp), 134.193, k36.338, 137.215, 138.433, 138.677, 139.067, 145.012, 155.636, 173.959, 176.104 (vinyl and ring carbons), 186.630 (carbene carbon), 200.227 (C≡O).

Preparation of Hexacarbonyltetrachlorodiosmium (112). This compound was prepared according to the method of Manchot and Konig.[38]

Preparation of bis-Dicarbonyl-η$^5$-cyclopentadienylosmium (113). This compound was prepared according to the method of Fischer et al; however, the yield was <5%, (lit 40%).[39]

Preparation of Phenylpropiolic Acid (135). Phenylacetylene (134) (10.21g, 0.100 mol) was dissolved in THF (100 mL) and cooled to 0°C via ice bath. A solution of n-BuLi (62.5 mL 1.6 M in hexane, 0.100 mol) was added at 3-4 drops/sec. The pale yellow phenylacetylene solution became opaque black towards completion of BuLi addition. The alkynyllithium solution was stirred for 30 min and then sprayed, via double-ended needle, into a 1000 mL Erlenmeyer flask containing 500g dry ice. The Erlenmeyer flask was continually flushed with dry nitrogen during the alkynyllithium addition to exclude moisture. Continuous stirring of the dry ice during alkynyllithium addition also kept spattering to a minimum. The slurry was allowed to come to room temperature, at which time solvent was removed in vacuo. The resulting solid was partitioned between saturated aqueous $Na_2CO_3$ solution (250 mL) and diethyl ether (2x250 mL). The aqueous phase was treated with 2.5 M HCl solution, extracted with $CHCl_3$ (2x200 mL), washed with water (3x200 mL), and dried with $MgSO_4$. After filtration and removal of solvent in vacuo, 12.6g (86%) white crystalline (135) was obtained. Recrystallization from $CCl_4$ (12.6g in 175 mL hot $CCl_4$) resulted in 10.5g 135; mp 136-136.5°C (lit 135°-136°C).[75]

Preparation of Methyl Phenylpropiolate (133). Phenylpropiolic acid (134)(5.0g, 34.21 mmol) was suspended in benzene (20 mL), to which was added thionyl chloride (5.0g, 42.03 mmol) and N,N-dimethylformamide (1 drop, catalyst). The solution was refluxed for 1.0 h and then cooled, filtered, and solvent removed in vacuo leaving the crude acid chloride as a pale yellow oil. The oil was then added to a solution of triethylamine (4.81 mL, 34.21 mmol, 1.0 eq. based on 134) in methanol at 0°C. After stirring for 30 min, the solution was partitioned between ether (100 mL) and $H_2O$ (100 mL). The ether layer was washed with 0.1 N HCl (50 mL), water 2x100 mLs), and finally dried over $MgSO_4$. After filtration and removal of solvent in vacuo, the oil was distilled (65°-66°C, 0.25 mm Hg) yielding 3.05g 133 as a colorless oil (56%). lit. bp 55°C, 0.22 mm Hg.[76]

Preparation of Methyl Z-2-Methoxycinnamate (131). This compound was prepared by the method of Wilson and Tebby or Wenkert et al., though the preparation by Wilson and Tebby was often contaminated with methyl E-2-methoxycinnamate (136).[43,44]

Preparation of Phenyldiazomethane (132). This compound was prepared by the method of Shecter et al.[45]

Attempted Preparation of Methyl 1-Methoxy-trans-2,3-diphenylcyclopropanecarboxylate (130). Phenyldiazomethane (132) (0.788g, 6.67 mmol) in THF (10 mL) was added dropwise to a refluxing solution of methyl Z-2-methoxycinnamate (131) (1.28g, 6.67 mmol) in THF (25 mL). After 12h reflux, the red color of the phenyldiazomethane gave way to the pale orange color of the diazine (142). By 60 MHz $^{1}H$ NMR analysis, the alkene (131) remained unchanged.

Preparation of Methyl 1-Bromo-1-methoxyacetate (145). Methyl methoxyacetate (137) (1.00g, 9.605 mmol) was dissolved in $CCl_4$ (10 mL) and heated to reflux with stirring. Bromine (1.535g, 9.605 mmol) in $CCl_4$ (10 mL) was added dropwise and reflux continued for 45 min (solution decolorizes). The solution was then allowed to cool and solvent removed in vacuo. Kugelrohr distillation (40°C, 0.050 mm Hg) resulted in collection of 1.60g (91%) colorless liquid (145); IR(neat) 2950(vs), 2850(vs), 1750(vs), 1430(vs), 1380(m), 1300(vs), 1220(vs), 1160(vs), 1100(vs), 1010(m), 860(m), 730(w), 550(s)$cm^{-1}$; $^{1}H$ NMR (100 MHz, $CDCl_3$) $\delta$ 3.59 (s,3H), 3.86(s,3H), 6.07(s,1H); $^{13}C$ NMR (25 MHz, $CDCl_3$) $\delta$ 52.778 ($OCH_3$), 58.286 ($OCH_3$). 83.092 (CH), 165.358 (C=O); mass spectrum m/e 181 ($M^+$). Anal. Calcd. for $C_4H_7BrO_3$: C,26.25; H,3.86. Found: C,26.33; H,3.90.

Preparation of Methyl 1-Bromo-1-methoxyacetate (145). Methyl methoxyacetate (137) (1.00g, 9.605 mmol) was dissolved in $CCl_4$ (10 mL) and heated to reflux with stirring. Bromine (1.535g, 9.605 mmol) in $CCl_4$ (10 mL) was added dropwise and reflux continued for 45 min (solution decolorizes). The solution was then allowed to cool and solvent removed in vacuo. Kugelrohr distillation (40°C, 0.050 mm Hg) resulted in collection of 1.60g (91%) colorless liquid (145); IR(neat) 2950 (vs), 2850(vs), 1750(vs), 1430(vs), 1380(m), 1300(vs), 1220(vs), 1160(vs), 1100(vs), 1010(m), 860(m), 730(w), 550(s)$cm^{-1}$; $^1H$ NMR (100 MJz, $CDCl_3$) δ3.59 (s,3H), 3.86 (s,3H), 6.07(s,1H); $^{13}C$ NMR (25 MHz, $CDCl_3$)δ52.778 ($OCH_3$), 58.286 ($OCH_3$), 83.092 (CH), 165.358 (C=O); mass spectrum m/e 181 ($M^+$). Anal. Calcd. for $C_4H_7BrO_3$: C,26.27; H,3.96. Found: C,26.33; H,3.90.

Attempted Generation of Bromocarbomethoxycarbene and Trapping with Trans-2-butene; Isolatin of t-Butyl 1-t-Butoxy-1-methoxyacetate (146). Potassium t-Butoxide (1.226g, 10.93 mmol) was placed in a 3-neck 100 mL roundbottom equipped with mechanical stirrer, septum, and nitrogen inlet. Trans-2-butene (40 mL) was condensed into the flask at -20°C. Stirring was commenced and methyl 1-bromo-1-methoxyacetate (145)(1.00g, 5.464 mmol) was added in via syringe. The solution was stirred at -20°C for 6 h. The reaction solution was then allowed to warm to room temperature after quenching

with $H_2O$ (5.0 mL). The solution was extracted with diethyl ether (3x25 mL), dired with $MgSO_4$, filtered, and solvent removed in vacuo. Column chromatography of the colorless oil (6"x 1", 230-400 mesh $SiO_2$) at 2.0 in/min resulted in isolation of 0.360g (15%) colorless oil (146); IR(neat) 2980(vs), 2860(sh), 1760(vs), 1460(m), 1380(vs), 1250(vs), 1200(vs), 1130(vs), 1060(vs), 980(s), 900(w), 850(s); $^1H$ NMR (100 MHz, $CDCl_3$) δ1.40(s,9H), 1.60(s,9H), 3.50(s,3H), 5.0(s,1H); $^{13}C$ NMR (25 MHz, $CDCl_3$)δ27.531 (t-Bu$CH_3$), 27.970 (t-Bu$CH_3$) 51.754($OCH_3$), 75.050 (t-BuC), 81.045 (t-BuC), 93.473(CH), 167.310 (C=O); mass spectrum m/e 218 ($M^+$, not observed), 145 (218-73), 73 (218-145). Anal. Calcd. for $C_{11}H_{22}O_4$:C,60.52; H,10.16. Found: C,60.41; H,10.20.

Preparation of Trans-2,3-dimethylthiophenylcyclopropane (151). This compound was prepared by the method of Boehe and Schneider[47] in 65% yield (lit. 80%).

Preparation of 1-Chloro-trans-2,3-diemthyl-1-thiophenyl-cyclopropane (162). Trans-2,3-dimethyl-1-thiophenylcyclo-propane (151)(4.00g, 22.43 mmol) was added to a suspension of 1,3,5-trichloroisocyanuric acid (1.95g, 8.40 mmol) in 50 mL $CCl_4$ at 0°C. The suspension was stirred for 2 h at o°C, and then allowed to warm to room temperature with an additional 3 h stirring. The suspension was filtered through a medium sintered-glass frit and then washed with water (3x50 mL). The organic phase was dried with $MgSO_4$, then filtered, and finally solvent was removed in vacuo

leaving a yellow oil. Kugelrohr distillation (80°C, 0.100 mm Hg) gave 3.95g (83%) of compound (151) as a colorless liquid; IR(neat) 3060(s), 2960(vs), 2930(vs), 2880(s), 1580(s), 1480(vs), 1440(vs), 1380(s), 1140(s), 1085(s), 1065(m), 1025(s),1005(m), 960(m), 940(m), 780(s), 740(vs), 685(vs)$cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ1.12 (p,1H, $^3J_{HH}$=7.07 Hz), 126 (d,3H, $^3J_{HH}$=5.84 Hz), 1.32-1.39 (pentent with overlaying doublet, 4H:p,1.35, $^3J_{HH}$= 6.12 Hz; d,1.36, $^3J_{HH}$= 6.16 Hz), 7.20-7.50(m,5H); $^{13}C$ NMR (25 MHz, $CDCl_3$) δ15.11 (cyclopropyl $C_2$ and $C_3$), 30.41 ($CH_3$), 56.97 (cyclopropyl $C_1$), 126.03 (para), 127.83 (ortho), 128.76 (meta), 135.14 (ipso); mass spectrum, m/e 212 ($M^+$). Anal. Calcd. for $C_{11}H_{13}ClS$: C,62.10; H,6.16. Found: C,61,95; H,6.16.

Preparation of 1-Methoxy-trans-2,3-dimethyl-1-thiophenylcyclopropane (165). The previously prepared 2-chlorothiophenylcyclopropane (162) (2.60g, 12.22 mmol) and $CdCO_3$ (2.32g, 13.44 mmol, 1.10 eq based on 162) were added to a 3-neck, 100 mL roundbottom flask containing 40 mL dry MeOH. The flask was equipped with a $CaSO_4$ drying tube, stopper, and solid addition funnel to which finely crushed $AgNO_3$ (2.49g, 14.66 mmol, 1.20 eq based on 162) had been added. The suspension was cooled to 0°C with stirring and the $AgNO_3$ was added in small portions over a 5 min period. Stirring was continued for 60 min as the yellow suspension darkened and was then allowed to warm to room temperature. The grey suspension was filtered through a medium sintered-glass frit and then solvent was removed in vacuo from the

resulting filtrate leaving a yellow oil. The oil was taken up in diethyl ether (100 mL) and then washed with water (3x100 mL). After drying the organic layer with $MgSO_4$ and subsequent filtration, solvent was removed in vacuo leaving a pale yellow oil. The oil was chromatographed on a silica gel column (MCB 230-400 mesh, 2"x 6") with ethyl acetate/hexane (1:99) at a flow rate of 2 in/min. Collection in 10 mL fractions and subsequent tlc analysis (pre-coated silica gel 60 F-254 plates, Merckcat. no. 5765-7, developed with ethyl acetate/hexane (10:90) resulted in combination of several fractions containing a compound with $R_f$=0.60. Removal of solvent in vacuo left 1.00g (40%) of colorless oil 165; IR(neat) 3060(w), 2980(m), 2950(s), 2930(s), 2860(m), 2820(w), 1590(s), 1475(s), 1440(m), 1210(w), 1190(w), 1150(s), 1100(s), 1050(m), 1020(m), 730(s), 680(s); $^1$H NMR (300 MHz, $CDCl_3$)$\delta$0.95 (oct,2H,$^3J_{HH}$=5.9 Hz), 1.17 (d,3H, $^3J_{HH}$=5.9 Hz), 1.22 (d,3H,$^3J_{HH}$=5.8 Hz), 3.38 (s,3H), 7.11 (t,1H,$^3J_{HH}$=7.2 Hz), 7.23 (t,2H,$^3J_{HH}$=7.4 Hz), 7.42 (d,2H, $^3J_{HH}$+7.9 Hz); $^{13}$C NMR (25 MHz, $CDCl_3$)$\delta$12.7 (cyclopropyl C), 15.1 (cyclopropyl C), 28.2 ($CH_3$), 30.0 ($CH_3$), 54.5 ($OCH_3$), 76.1 (quat. C), 125.2 (para), 127.9 (ortho), 128.5 (meta), 136.3 (ipso); mass spectrum, m/e 208 ($M^+$), Anal. Calcd. for $C_{12}H_{16}OS$: C,69.19; H,7 74. Found: C,69.06; H,7.78.

Preparation of 1-Methoxy-trans-2,3-dimethylcyclopropane-1-carboxylic acid (126). Lithium ribbon (0.069g, 10.08 mmol) was cut into 5-10 mg slivers and placed in a 3-neck 100 mL roundbottom flask equipped with a nitrogen inlet, high speed mechanical stirrer (glass), and rubber septum. Napthalene (1.29g, 10.08 mmol) was added to the flask, followed by 30 mL THF. The solution was then stirred at room temperature for 24 h and subsequently cooled to -78°C. The mixed ketal 165 (1.00g, 4.80 mmol) in THF (2.0 mL) was added via syringe to the green-black lithium naphthalenide solution at -78°C. After stirring for 1.0 h at -50°C, the solution was allowed to warm to -20°C until the green-black color of the lithium naphthalenide solution gave way to the orange-red color of the α-methoxylithiocyclopropane 167. After stirring for an additional 30 min at this temperature, the solution was then cooled to -78°C and blanketed with $CO_2$ via needle inlet, which resulted in total decolorization of the solution within 15 sec. The solution was allowed to warm to room temperature with stirring over a 2 h period. Solvent was removed in vacuo and the residue partitioned between diethyl ether (50 mL) and 1.2M aq HCl (50 mL). The ether layer was washed with 5% $NaHCO_3$ (3x50 mL) and then the combined $NaHCO_3$ fractions were washed with ether (3x50 mL). Careful acidification of the $NaHCO_3$ layer with 1.2M aq HCl resulted in a formation of a white supension, to which was added saturated aqueous

NaCl solution (10 mL). The aqueous layer was extracted with ether (2x50 mL). The organic phase was dried with $MgSO_4$, filtered, and the solvent removed in vacuo leaving a pale yellow oil. Kugelrohr distillation (70 C, 0.050 mm Hg) resulted in 0.575g (83%) of white, crystalline 126: mp 47.0°-48.0°C; IR(neat) 3500-2800 (br), 1690(vs), 1430(s), 1320(m), 1280(s), 1230(s), 1150(s), 1110(m), 1080(m), 910(m), 815(s), 730(s)$cm^{-1}$; $^1H$ NMR (100 MHz, $CDCl_3$) δ1.10-1.22(m,7H), 1.44-1.56(m,1H), 3.47(s,3H), 11.69(s,1H); $^{13}C$ NMR (25 MHz, $CDCl_3$) δ11.99 (cyclopropyl C), 12.19 (cyclopropyl C), 30.90 ($CH_3$), 31.19 ($CH_3$), 57.51 ($OCH_3$), 67.64 (quat C), 179.05 (carboxyl C); mass spectrum m/e 144 ($M^+$). Anal. Calcd. for $C_7H_{12}O_3$: C,58.32; H,8.39. Found: C,58.10; H,8.41.

Preparation of 1-Methoxy-trans-2,3-dimethylcyclopropane-1-carbonyl Chloride (168). The 1-methoxy-trans-2,3-dimethylcyclopropane-1-carboxylic acid 126 (0.835g, 5.79 mmol) was dissolved in diethyl ether (20 mL). Thionyl chloride (0.50 mL, 3.5 eq) was added to the solution, followed by N,N-diemthylformamide (1.0 drop). The solution was refluxed for 10 h. The pale yellow solution was filtered and the solvent was removed in vacuo, resulting in 0.700g (74%) yellow oil (168): IR(neat) 2960(s), 2940(s), 2840(m), 1780 (vs), 1450(s), 1320(s), 1250(vs), 1120(m), 1065(s), 1040(s), 940(m), 830(m), 770(s), 620(m)$cm^{-1}$; $^1H$ NMR (100 MHz, $CDCl_3$) δ1.209 (t,6H, $^3J_{HH}$=6.71 Hz), 1.302-1.774 (m,2H), 3.515(s,3H);

$^{13}C$ NMR (25 MHz, $CDCl_3$) δ11.702 (cyclopropyl C), 12.579 (cyclopropyl C), 33.921 ($CH_3$), 34.213 ($CH_3$), 58.385 ($OCH_3$), 74.661 (cyclopropyl $C_1$), 175.051 (C=O).

Preparation of Dicarbonyl-$\eta^5$-cyclopentadienyl(1-methoxy-trans-2,3-dimethylcyclopropyl-1-carbonyl)iron (125). Potassium dicarbonyl-$\eta^5$-cyclopentadienylferrate (0.893g, 4.13 mmol) was suspended in THF (10 mL) and cooled to -78°C with stirring. The 1-methoxy-trans-2,3-dimethyl-cyclopropane-1-carbonyl chloride 168 (0.672g, 4.13 mmol) in THF (10 mL) was added to the cold (-78°C) suspension of KFp via syringe over a 5 min period. The solution was allowed to warm to room temperature and continue stirring 12 h. Solvent was removed in vacuo and the residue was extracted with benzene (3x15 mL). The extracts were filtered through a Celite mat on a coarse, sintered-glass frit and, after silica gel (3.0g, 60-200 mesh) was added, the solvent was removed in vacuo. The resulting brown solid was placed on a 1"x 6" silica gel column (230-400 mesh, prepared with $CH_2Cl_2$/hexane, 60% v/v) and eluted at 2.0 in/min. $Fp_2$ eluted immediately, while the acyl complex remained at the top of the column. After collection of the purple $Fp_2$ band, elution was continued with ethyl acetate/hexane (50% v/v) which resulted in the collection of an orange band. Removal of solvent in vacuo and recyrstallization from $CH_2Cl_2$/hexane (as in the preparation of RppCl) resulted in 0.567g (48%) air=stable, orange, crystalline

acyl complex 125: mp 61.0-62.0°C; IR($CDCl_3$)νco 2000(vs), 1950(vs), 1650(s)$cm^{-1}$; $^1H$ NMR (100 MHz, benzene-$d_6$)δ 0.990-1.446(m,7H),1.514(g,1H,$^3J_{HH}$=6.51 Hz), 3.165(s,3H), 4.256(s,5H); $^{13}C$ NMR (25 MHz, benzene-$d_6$) δ12.803 (cyclopropyl C), 13,680 (cyclopropyl C), 26.929 ($CH_3$), 30.826 ($CH_3$), 57.535 ($OCH_3$), 86.577 (cyclopropyl $C_1$), 215.524 (C≡O), 216.011 (C≡O), 255.875 (-C=O); mass spectrum, m/e 276 ($M^+$-CO), 248 ($M^+$-2CO), 205 ($FpCO^+$), 99 ($M^+$-FpCO. Anal. Calcd. for $C_{14}H_{16}O_4Fe$: C,55.29; H,5.30. Found: C,55.41; H,5.35.

Preparation of Dicarbonyl-η$^5$-cyclopentadienyl(1-methoxy-trans-2,3-dimethylcyclopropan-1-yl)iron (122). Acyl complex (125)(0.800g, 2.63 mmol) and rhodium complex (174)(3.5g, 2.63 mmol, 2.0 equivalents) were suspended in degassed acetonitrile (50 mL) and stirred over a 48 h period at 25°C. The solution was filtered and solvent removed in vacuo. The residue was taken up in the minimum amount of ethyl acetate-hexane (10:90 v/v) and placed on a 1"x 6" silica gel column (230-400 mesh, prepared with ethyl acetate-hexane, 10:90 v/v). Elution at the rate of 2"/min resulted in the collection of a single yellow band. Removal of solvent in vacuo gave 0.247g (34%) viscous yellow oil (122). IRνco 2000(vs), 1940(vs) $cm^{-1}$; $^1H$ NMR (300 MHz, benzene-$d_6$) δ0.192 (p,1H,$^3J_{HH}$=6.49 Hz), 0.268(p,1H, $^3J_{HH}$=6.17 Hz), 1.005(d,3H,$^3J_{HH}$=6.22 Hz), 1.053 (d,3H, $^3J_{HH}$=5.90 Hz), 2.812(s,3H), 4.061(s,5H); $^{13}C$ NMR (25 MHz, $CD_2Cl_2$) δ 14.376 ($CH_3$), 18.275 ($CH_3$), 29.287 (CH),

35.818(CH), 56.431 ($OCH_3$), 77.581 (quat. C), 87.328 (Cp), 218.127 (C≡O), 218.517 (C≡O); mass spectrum m/e 276 ($M^+$).

Preparation of ($\eta^2$-1,3-Dimethylallene)dicarbonyl-$\eta^5$-cyclopentadienyliron Trifluoromethanesulfonates (179) and (180). Sigma complex (122)(0.125g, 0.453 mmol) was dissolved in solvent (10 mL, either methylene chloride or cyclohexene) and cooled to -78°C with stirring. Trimethylsilyltrifluoromethanesulfonate (0.200g, 0.905 mmol, 2.0 eq) was added to the stirred solution dropwise. Upon addition of the TMSOTF, yellow crystalline (179)and (180) precipitated immediately. The suspension was allowed to warm to room temperature at which point solvent was removed in vacuo. The residue was extracted with methylene chloride (2.0 mL) and filtered through Celite (0.1g) in a pipette. The filtrate was added dropwise slowly to ether (30 mL), with constant swirling, giving a yellow precipitate. The suspension was filtered, washed with ether (2x10 mL), and placed under vacuum overnight giving 0.180g (100%) yellow crystalline 179 and 180. mp 87.0-88.0°C; IRνco 2070(s), 2020(s) $cm^{-1}$; $^1H$ NMR (300 MHz, $CD_2Cl_2$) δ:(anti isomer) 1.633 (d,3H, $^3J_{HH}$=6.28 Hz), 2.078 (dof d,3H, $^3J_{HH}$=6.90 Hz, $^5J_{HH}$=2.23 Hz), 4.371 (m,1H), 5.634(s,5H), 6.157(m,1H); (syn isomer) 1.590 (d,3H, $^3J_{HH}$=6.22 Hz), 2.226 (d of d, 3H, $^3J_{HH}$=6.9 Hz, $^5J_{HH}$=2.64 Hz), 4.351 (m,1H), 5.699 (s,5H),

6.755 (m,1H); $^{13}C$ NMR (75 MHz, $CD_3NO_2$) δ:(anti isomer) 19.862 ($CH_3$), 20.934 ($CH_3$), 44.183 (CH), 92.237 (Cp), 129.000 (CH), 151.356 (=C=), 209.876 (C≡O); syn isomer 18.157 ($CH_3$), 42.100 (CH), 92.042 (Cp), 113.828 (CH), 152.526 (=C=), 209.876 (C≡O). Anal. Calcd. for $C_{13}H_{13}O_5F_3FeS$: C,39.62; H,3.32. Found:

Preparation of 2-(carbonyl-$\eta^5$-cyclopentadienyliron)-3-methoxy-trans-4,5-dimethylcyclopent-2-en-1-one (172). Acyl complex 125 (1.00g, 3.29 mmol) was dissoved in dry, degassed benzene (10 mL) in a 1/2" x 10" Pyrex photolysis tube equipped with boiling chip and septum with needle inlet. The tube was placed in a photolysis well approximately 6" from a 450 W medium pressure Hg lamp. After cooling the solution to 15°-20°C, photolysis was initiated and continued for 6 h. Solvent was removed in vacuo and the residue was taken up in the minimum amount of ethyl acetate-pentane (10:90 v/v) and placed on a 1"x 6" silica gel column (230-400 mesh, prepared with ethyl acetate-hexane, 10:90 v/v). Elution with ethyl acetate-hexane (10:90 v/v) resulted in the separation of several yellow-colored bands initially, however, after 200 mL eluent a brown band followed by an orange-red band was observed. Collection of the orange-red band and removal of the solvent in vacuo resulted in 0.180g (20%) red cyrstalline 172. mp 79.5-80.0°C; IRνco 1950(s), 1625(m) $cm^{-1}$; $^1H$ NMR (300 MHz, benzene-$d_6$) δ 0.936 (d,3H, $^3J_{HH}$=6.89 Hz), 1.085 (d,3H, $^3J_{HH}$=7.01 Hz), 1.926

(p,1H, $^{3}J_{HH}$=7.01 Hz), 2.109 (p,1H, $^{3}J_{HH}$=7.18 Hz), 3.739 (s,3H), 4.353(s,5H); $^{13}$C NMR (75 MHz, benzene-$d_6$) δ 15.824 ($CH_3$), 16.799 ($CH_3$), 63.871 (CH), 66.210 ($OCH_3$), 69.037 (CH), 86.480 (Cp), 216.783 (C≡O), 269.249 (C=O), 348.088 (carbene C); mass spectrum m/e 276 ($M^+$). Anal. Calcld. For $C_{13}H_{16}O_3Fe$: C,56.29; H,5.91.

Resolution of (±) 1-Methoxy-trans-2,3-dimethylcyclopropane Carboxylic Acid (126). Racemic acid (126) (0.500g, 3.46 mmol) and (-) quinine (1.125g, 3.46 mmol) were dissolved in hot ethanol (25 mL) and allowed to slowly cool to room temperature, at which time the solution was placed in the refrigerator (10°C) for 2 days and then in the freezer (-5°C) for 4 days. The resulting white crystals were isolated by rapid vacuum filtration and washing with cold thanol (2x10 mL). After air drying, 0.536g (33%) white crystalline diastereomer was obtained. mp 202-205°C (dec). The white solid was then partitioned between ether (50 mL) and 1.0 N HCl (50 mL) and the ether layer was washed with 1.0 N HCl (2x50 mL). The ether solution was dried with $MgSO_4$, filtered, and then the solvent was removed in vacuo yielding 0.150g (30%) of acid (126), $[\alpha]_D^{25}$= -17.46° (c=0.24, absolute ethanol), with identical $^{1}$H NMR and IR as racemic acid (126).

Preparation of Optically Active 1-Methoxy-trans-2,3-dimethylcyclopropane-1-carbonyl Chloride (168). This compound was prepared in the exact manner as listed for the racemic acid chloride (168) using optically acitve acid (126).

Preparation of Optically Active Dicarbonyl-$\eta^5$-cyclopentadienyl(1-methoxy-trans-2,3-dimethylcyclopropyl-1-carbonyl)iron (125). This compound was prepared in the exact manner as racemic acyl complex (125) using optically active acid chloride (168).

Preparation of Optically Active Dicarbonyl-$\eta^5$-cyclopentadienyl (1-methoxy-trans-2,3-diemthylcyclopropan-1-yl) iron (122). This compound was prepared in the exact manner as racemic sigma complex (122) using optically active acyl complex (125).

Determination of Optical Purity of Optically Active Dicarbonyl-$\eta^5$-cyclopentadienyl(1-methoxy-trans-2,3-dimethylcyclopropyl-1-carbonyl)iron (125). (-)Eu(hfc)$_3$ (186) (0.500g, 0.419 mmol) was dissolved in 5.0 mL benzene-$d_6$. Racemic acyl complex (125) (0.127g, 0.419 mmol) was also dissolved in 5.0 mL benzene-$d_6$. As shown in Figure 17, using $^1$H NMR (100 MHz), a sample of pure racemic acyl complex solution gave rise to spectrum A. A sample of racemic acyl complex solution (0.5 mL) and (-)Eu(hfc)$_3$ solution (0.005 mL) gave rise to spectrum B (acyl complex with 1.0 mole % shift reagent). A sample of racemic acyl complex solution

(0.5 mL) and (-)Eu(hfc)$_3$ solution (0.025 mL) gave rise to spectrum C (acyl complex with 5.0 mole% shift reagent). To determine the optical purity of optically active acyl complex (125), the optically active acyl complex (125) (0.063g in 0.4 mL benzene-$d_6$) and (-)Eu(hfc)$_3$ solution (0.1 mL) gave rise to the $^1$H NMR spectrum shown in Figure 18.

Preparation of ($\eta^2$-1,3-Dimethylallene)dicarbonyl-$\eta^5$-cyclopentadienyliron Trifluoromethanesulfonates (179) and (180) from Optically Active Dicarbonyl-$\eta^5$-cyclopentadienyl (1-methoxy-trans-2,3-dimethylcyclopropan-1-yl)iron (122). Optically active sigma complex (122) (0.110g, 0.398 mmol) was dissolved in methylene chloride (10 mL) and cooled to -78$^o$C. TMSOTF (0.176g, 2.0 eq) was added dropwise slowly to the stirred solution, which was then allowed to warm to room temperature. Work-up was accomplished in the exact manner as described for preparation of racemic (179) and (180), resulting in isolation of 0.170g (92%) (179) and (180) showing identical $^1$H NMR as (179) and (180) prepared from racemic sigma complex (179) and (180). To determine the specific rotation of allene complexes (179) and (180) prepared from optically active sigma complex (122), the allene complexes (179) and (180)(0.065g, 1.65 mmol) were dissolved in 5.0 mL $CH_2Cl_2$. At $\lambda$=589 nm, no rotation was observed, i.e. $[\alpha]=0.000\pm0.001$ therefore $[\alpha]_D^{25}\leq 0.200$.

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James Raymond Lisko was born July 12, 1954, in Elkins, West Virginia, while his parents were attending and living on the campus of Davis and Elkins College. As his father was a pilot in the United States Air Force, Jim's youth was spent moving from one locale to another.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William M. Jones
Chairman
Professor of Chemistry

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William R. Dolbier
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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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